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(54) **ELECTRICALLY CONDUCTIVE PROPPANT**

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    See application file for complete search history.

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(57) **ABSTRACT**

Electrically conductive sintered, substantially round and spherical particles and methods for producing such electrically conductive sintered, substantially round and spherical particles from an alumina-containing raw material. Methods for using such electrically conductive sintered, substantially round and spherical particles in hydraulic fracturing operations.

12 Claims, 10 Drawing Sheets

Related U.S. Application Data

is a continuation of application No. 14/147,372, filed on Jan. 3, 2014, now Pat. No. 8,931,553, which is a continuation of application No. PCT/US2014/010228, filed on Jan. 3, 2014.

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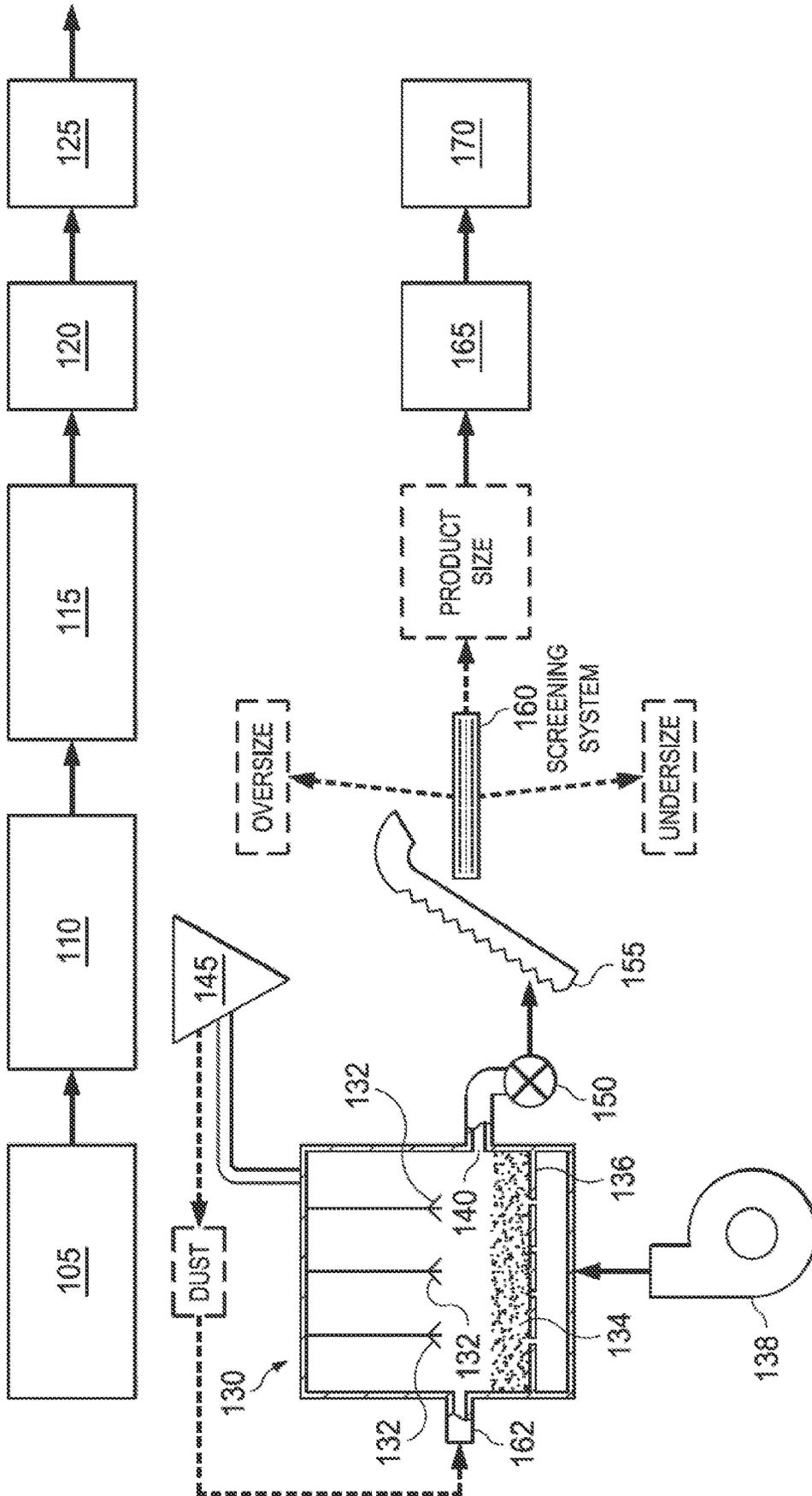|			
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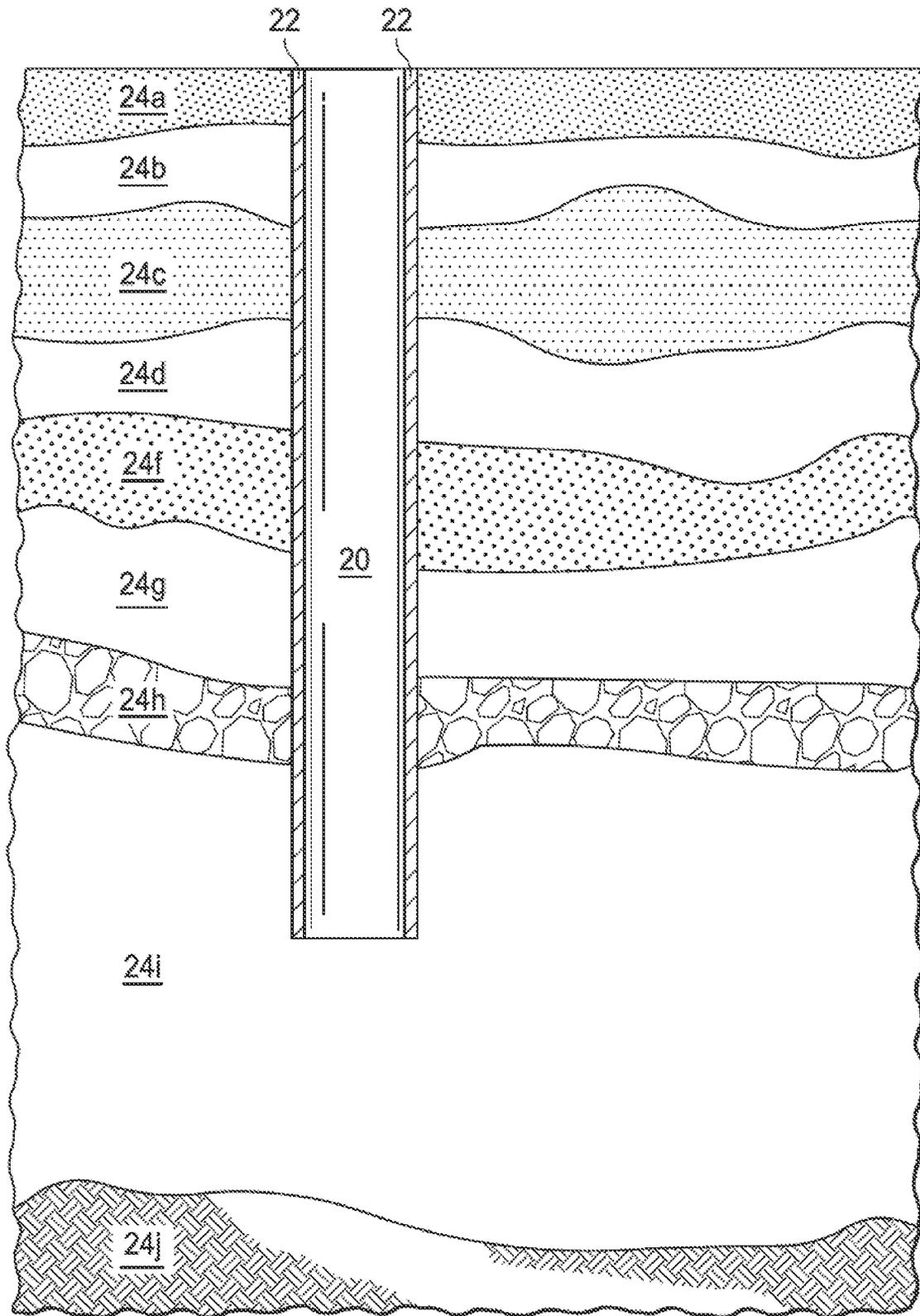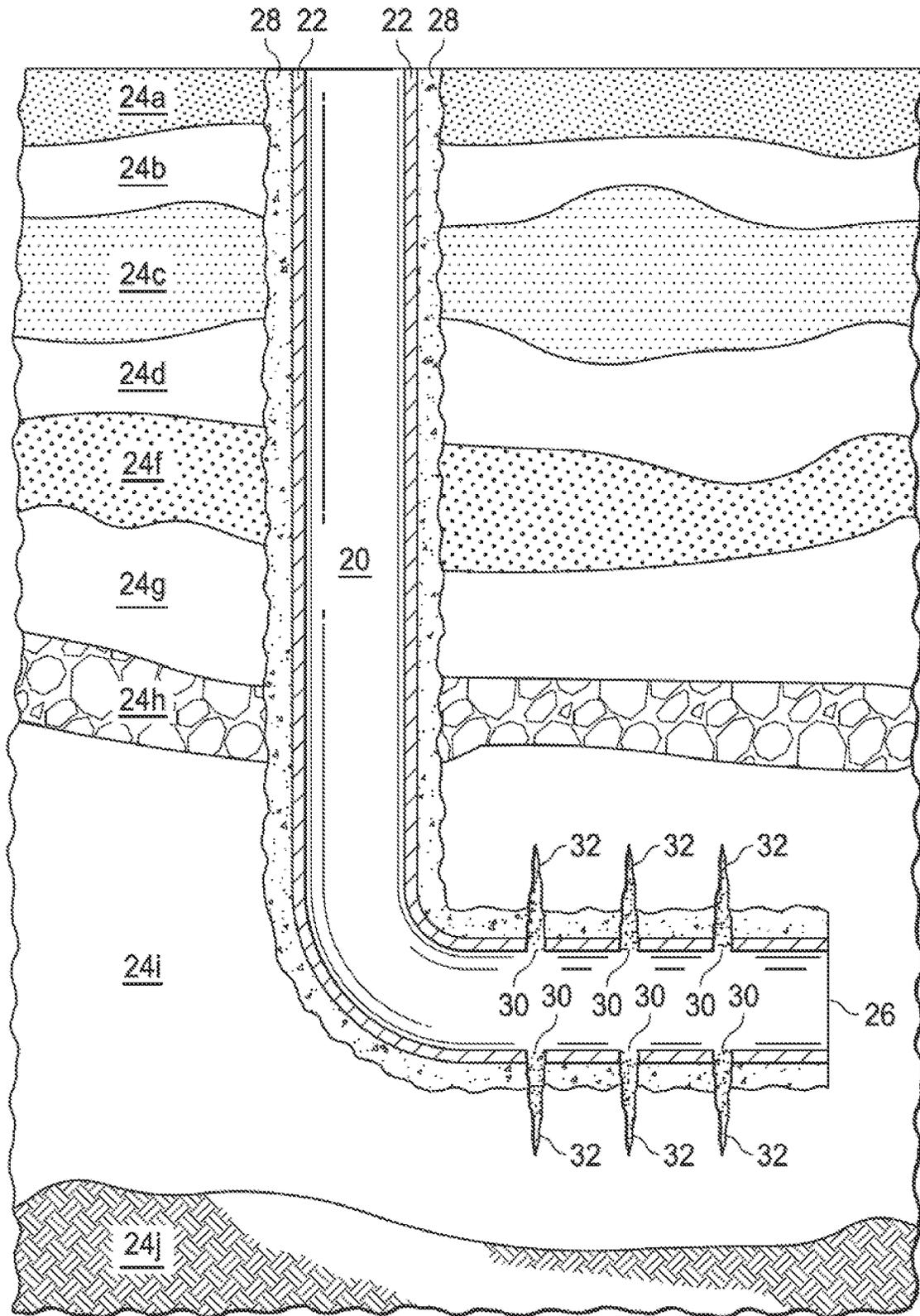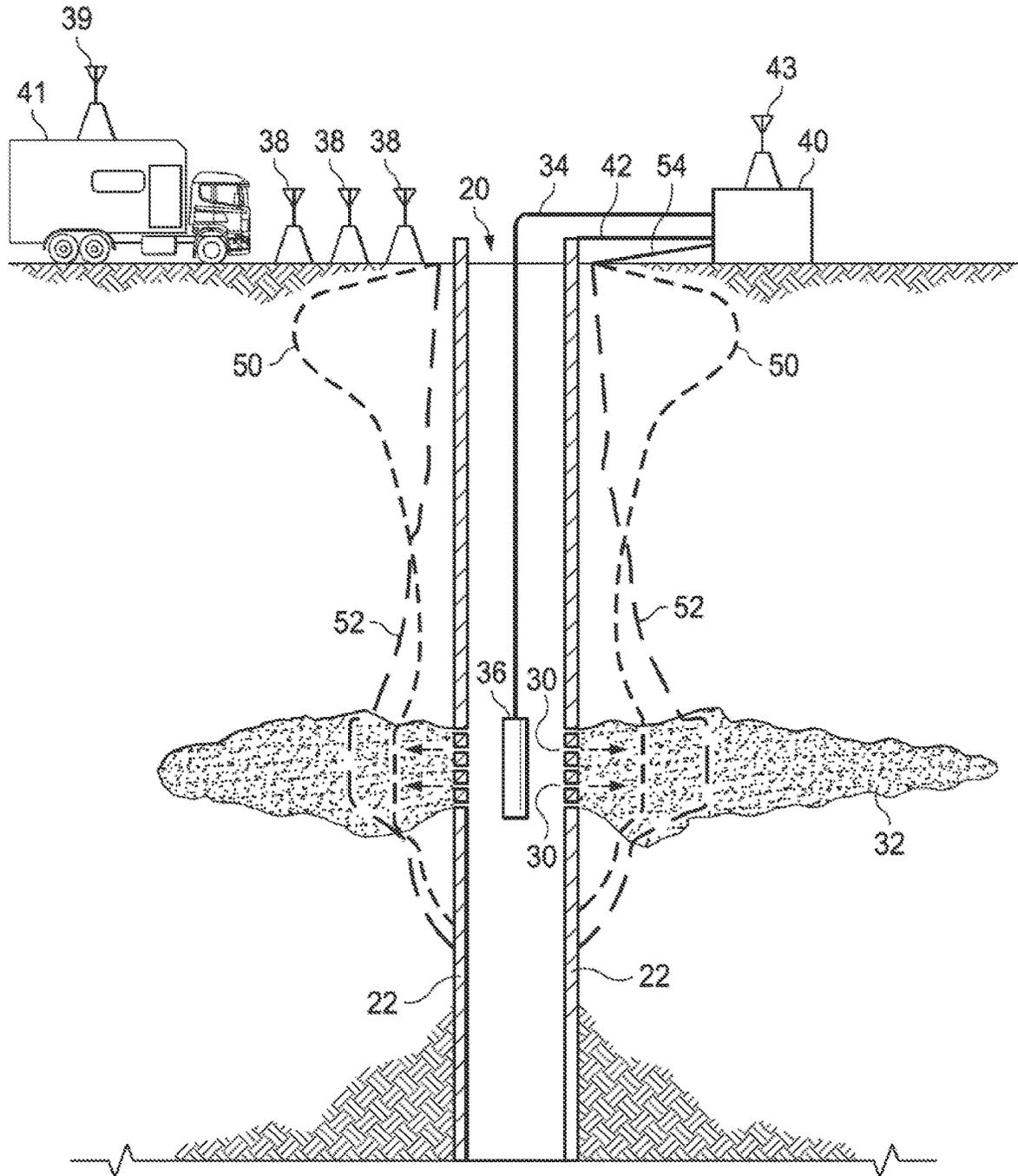
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Fig. 1

| 105 | 110 | 115 | 120 | 125 |

| 160 | PRODUCT SIZE | 165 | 170 |

OVERSIZE

UNDERSIZE

SCREENING SYSTEM

DUST

145

155

150

130

132

140

132

132

136

134

138

162

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7A

Fig. 7B

Fig. 8

200

226

228

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232

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204 212

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Fig. 9

Legend:
- CL WITH 0.1% PEDOT
- CL WITH 500 nm Al COAT
- CL WITH 0.1% PEDOT/ AMINO SILANE
- CL WITH 0.4% PEDOT/ AMINO SILANE
- CL WITH 500 nm Al COAT
- CL WITH 100 nm Al COAT
- HP WITH 500 nm Al COAT
- HP WITH 100 nm Al COAT
- CL WITH 0.4% PEDOT

RESISTIVITY (Ohm-cm)

PRESSURE (psi)

Fig. 10

Fig. 11

ELECTRICALLY CONDUCTIVE PROPPANT

CROSS-REFERENCE TO RELATED PATENT APPLICATIONS

This application is a continuation-in-part of U.S. patent application Ser. No. 14/593,447 filed on Jan. 9, 2015, which is a continuation of U.S. patent application Ser. No. 14/147,372 filed on Jan. 3, 2014 and International Patent Application No. PCT/US2014/010228 filed Jan. 3, 2014, each of these prior applications being incorporated herein by reference in its entirety. U.S. patent application Ser. No. 14/593,447, U.S. patent application Ser. No. 14/147,372, and International Patent Application No. PCT/US2014/010228 each claims the benefit of U.S. Provisional Patent Application No. 61/749,093 filed Jan. 4, 2013 which is incorporated herein by reference in its entirety.

STATEMENT OF GOVERNMENTAL INTEREST

This invention was made under a CRADA (SC11/01780.00) between CARBO Ceramics, Inc. and Sandia National Laboratories, operated for the United States Department of Energy. The Government has certain rights in this invention.

BACKGROUND

Embodiments of the present invention relate generally to hydraulic fracturing of geological formations, and more particularly to electromagnetic (EM) methods for detecting, locating, and characterizing electrically conductive proppants used in the hydraulic fracture stimulation of gas, oil, or geothermal reservoirs. The methods described herein involve electrically energizing the earth at or near a fracture at the depth of the fracture and measuring the electric and magnetic field responses at the earth's surface or in adjacent wells/boreholes. Other embodiments of the present invention relate to compositions and methods for the formation of the electrically conductive proppants for use in the electromagnetic methods for detecting, locating and characterizing such proppants.

In order to stimulate and more effectively produce hydrocarbons from downhole formations, especially formations with low porosity and/or low permeability, induced fracturing (called "frac operations", "hydraulic fracturing", or simply "fracing") of the hydrocarbon-bearing formations has been a commonly used technique. In a typical frac operation, fluids are pumped downhole under high pressure, causing the formations to fracture around the borehole, creating high permeability conduits that promote the flow of the hydrocarbons into the borehole. These frac operations can be conducted in horizontal and deviated, as well as vertical, boreholes, and in either intervals of uncased wells, or in cased wells through perforations.

In cased boreholes in vertical wells, for example, the high pressure fluids exit the borehole via perforations through the casing and surrounding cement, and cause the formations to fracture, usually in thin, generally vertical sheet-like fractures in the deeper formations in which oil and gas are commonly found. These induced fractures generally extend laterally a considerable distance out from the wellbore into the surrounding formations, and extend vertically until the fracture reaches a formation that is not easily fractured above and/or below the desired frac interval. The directions of maximum and minimum horizontal stress within the formation determine the azimuthal orientation of the

induced fractures. Normally, if the fluid, sometimes called slurry, pumped downhole does not contain solids that remain lodged in the fracture when the fluid pressure is relaxed, then the fracture re-closes, and most of the permeability conduit gain is lost.

These solids, called proppants, are generally composed of sand grains or ceramic particles, and the fluid used to pump these solids downhole is usually designed to be sufficiently viscous such that the proppant particles remain entrained in the fluid as it moves downhole and out into the induced fractures. Prior to producing the fractured formations, materials called "breakers", which are also pumped downhole in the frac fluid slurry, reduce the viscosity of the frac fluid after a desired time delay, enabling these fluids to be easily removed from the fractures during production, leaving the proppant particles in place in the induced fractures to keep them from closing and thereby substantially precluding production fluid flow there through.

The proppants may also be placed in the induced fractures with a low viscosity fluid in fracturing operations referred to as "water fracs" or "slick water fracs". The fracturing fluid in water fracs is water with little or no polymer or other additives. Water fracs are advantageous because of the lower cost of the fluid used. Also when using cross-linked polymers, it is essential that the breakers be effective or the fluid cannot be recovered from the fracture, effectively restricting flow of formation fluids. Water fracs, because the fluid is not cross-linked, do not rely on the effectiveness of breakers.

Commonly used proppants include naturally occurring sands, resin coated sands, and ceramic proppants. Ceramic proppants are typically manufactured from naturally occurring materials such as kaolin and bauxitic clays, and offer a number of advantages compared to sands or resin coated sands principally resulting from the compressive strength of the manufactured ceramics and their highly spherical particle shape.

Although induced fracturing has been a highly effective tool in the production of hydrocarbon reservoirs, the amount of stimulation provided by this process depends to a large extent upon the ability to generate new fractures, or to create or extend existing fractures, as well as the ability to maintain connection to the fractures through appropriate placement of the proppant. Without appropriate placement of the proppant, fractures generated during the hydraulic fracturing may tend to close, thereby diminishing the benefits of the hydraulic fracturing treatment. However, reliable methods for detecting, locating and characterizing the placement of proppant within fractures at relatively far distances from the wellbore and thus confirming whether or not such placement has been appropriate are not available.

Current state of the art proppant identification techniques are limited to relatively short distances (12 inches to 18 inches maximum) from the wellbore. Radioactive and non-radioactive tracers and proppants are currently used to infer the presence of proppant in the near well bore region. A better understanding of proppant placement in the far field regions of a hydraulic fracture is needed.

Previous work for massive hydraulic fracture mapping is summarized in Bartel, L. C., McCann, R. P., and Keck, L. J., Use of potential gradients in massive hydraulic fracture mapping and characterization, prepared for the 51st Annual Fall Technical Conference and Exhibition of Society of Petroleum Engineers, New Orleans, Oct. 3-6, 1976 paper SPE 6090. In this previous work, the electric potential differences were measured between two concentric circles of voltage electrodes around a vertical fracture well at the earth's surface. The well was electrically energized at the top

of the well casing or at the depth of the fracture. The electrical ground was established at a well located at a distance of approximately one mile from the fracture well. At that time, the fact that the grounding wire acted as a transmitting antenna was not taken into account. The water used for the fracture process contained potassium chloride (KCl) to enhance its electrical conductivity and the fracture was propped using non-conducting sand. A 1 Hz repetition rate square wave input current waveform was used and only the voltage difference amplitudes were measured. Voltages using an elementary theory based on current leakage from the well casing and the fracture into a homogeneous earth were used to produce expected responses. Comparing the field data to results from the elementary model showed that a fracture orientation could be inferred, however, since the model did not account for the details of the fracture, other fracture properties could not be determined using the elementary model.

A method of detecting, locating and characterizing the location of the proppant as placed in a hydraulic fracture at distances of more than several inches from the cased well-bore is currently unavailable. Such a method for detecting, locating and characterizing the proppant material after the proppant material is placed in a fracture would be beneficial.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention may best be understood by referring to the following description and accompanying drawings that are used to illustrate embodiments of the invention. In the drawings:

FIG. 1 is a schematic illustration of a system for preparing substantially round and spherical particles from a slurry as described herein.

FIG. 2 is a diagram of the geometric layout of a vertical or deviated well in which layers of the earth having varying electrical and mechanical properties are depicted.

FIG. 3 is a schematic of an installed horizontal wellbore casing string traversing a hydrocarbon bearing zone with proppant filled fractures in which layers of the earth having varying electrical and mechanical properties are depicted.

FIG. 4 is a schematic cross-sectional illustration of a hydraulic fracture mapping system which depicts two embodiments for introducing electric current into a well-bore, namely energizing the wellbore at the surface and energizing via a wireline with a sinker bar near perforations in the wellbore.

FIG. 5 is a schematic plan illustration of a hydraulic fracture mapping system.

FIG. 6 is a schematic perspective illustration of a hydraulic fracture mapping system.

FIG. 7A is a schematic illustration of an electrically insulated casing joint.

FIG. 7B is a schematic illustration of an electrically insulated casing collar.

FIG. 8 is schematic illustration of a test system for measuring proppant electrical resistance.

FIG. 9 is a graph of resistivity (Ohm-cm) vs. Closure Pressure (psi) for various proppant samples.

FIG. 10 is a graph of resistivity (Ohm-cm) vs. Closure Pressure (psi) for mixtures of CARBOLite 20/40 coated with aluminum and standard EconoProp 20/40 samples.

FIG. 11 is a graph of resistivity (Ohm-cm) vs. Closure Pressure (psi) for mixtures of Hydroprop 40/80 coated with aluminum and standard Hydroprop 40/80 samples.

DETAILED DESCRIPTION

In the following description, numerous specific details are set forth. However, it is understood that embodiments of the

invention may be practiced without these specific details. In other instances, well-known structures and techniques have not been shown in detail in order not to obscure the understanding of this description.

Described herein are electromagnetic (EM) methods for detecting, locating, and characterizing electrically conductive proppants used in the hydraulic fracture stimulation of gas, oil, or geothermal reservoirs. Also described herein are electrically conductive sintered, substantially round and spherical particles and methods for preparing such electrically conductive sintered, substantially round and spherical particles from a slurry of an alumina containing raw material for use as proppants in the electromagnetic methods. The term "substantially round and spherical" and related forms, as used herein, is defined to mean an average ratio of minimum diameter to maximum diameter of about 0.8 or greater, or having an average sphericity value of about 0.8 or greater compared to a Krumbein and Sloss chart.

According to embodiments of the present invention, the electrically conductive sintered, substantially round and spherical particles, referred to hereinafter as "electrically conductive proppant" may be made from a conventional proppant such as a ceramic proppant, sand, plastic beads and glass beads. Such conventional proppants may be manufactured according to any suitable process including, but not limited to continuous spray atomization, spray fluidization, spray drying, or compression. Suitable conventional proppants and methods for their manufacture are disclosed in U.S. Pat. Nos. 4,068,718, 4,427,068, 4,440,866, 5,188,175, and 7,036,591, the entire disclosures of which are incorporated herein by reference.

Ceramic proppants vary in properties such as apparent specific gravity by virtue of the starting raw material and the manufacturing process. The term "apparent specific gravity" as used herein is the weight per unit volume (grams per cubic centimeter) of the particles, including the internal porosity. Low density proppants generally have an apparent specific gravity of less than 3.0 g/cm^3 and are typically made from kaolin clay and other alumina, oxide, or silicate ceramics. Intermediate density proppants generally have an apparent specific gravity of about 3.1 to 3.4 g/cm^3 and are typically made from bauxitic clay. High strength proppants are generally made from bauxitic clays with alumina and have an apparent specific gravity above 3.4 g/cm^3.

An electrically conductive material such as a metal, a conductive polymer, or a conductive particle may be added at any suitable stage in the manufacturing process of any one of these proppants to result in an electrically conductive proppant suitable for use according to certain embodiments of the present invention. The electrically conductive material can also be added to any one of these proppants after manufacturing of the proppants. In one or more exemplary embodiments, the proppant can be a porous proppant, such that the electrically conductive material can be impregnated or infused into the pores of the proppant to provide the electrically conductive proppant. The porous proppant can be impregnated or infused with the electrically conductive material in any suitable amounts, such as from about 1% to 15% by weight. Water soluble coatings such as polylactic acid can be used to coat these particles to allow for delayed/timed release of conducting particles.

According to certain embodiments of the present invention, the electrically conductive material is coated onto the proppants. The coating may be accomplished by any coating technique well known to those of ordinary skill in the art such as spraying, sputtering, vacuum deposition, dip coat-

ing, extrusion, calendaring, powder coating, transfer coating, air knife coating, roller coating and brush coating.

According to certain embodiments of the present invention, the electrically conductive material is incorporated into a resin material and ceramic proppant or natural sands are coated with the resin material containing the electrically conductive material. Processes for resin coating proppants and natural sands are well known to those of ordinary skill in the art. For example, a suitable solvent coating process is described in U.S. Pat. No. 3,929,191, to Graham et al., the entire disclosure of which is incorporated herein by reference. Another suitable process such as that described in U.S. Pat. No. 3,492,147 to Young et al., the entire disclosure of which is incorporated herein by reference, involves the coating of a particulate substrate with a liquid, uncatalyzed resin composition characterized by its ability to extract a catalyst or curing agent from a non-aqueous solution. Also a suitable hot melt coating procedure for utilizing phenol-formaldehyde novolac resins is described in U.S. Pat. No. 4,585,064, to Graham et al, the entire disclosure of which is incorporated herein by reference. Those of ordinary skill in the art will be familiar with still other suitable methods for resin coating proppants and natural sands.

As described herein, sintered, substantially round and spherical particles, or proppants, are prepared from a slurry of alumina-containing raw material. In certain embodiments, the particles have an alumina content of from about 40% to about 55% by weight. In certain other embodiments, the sintered, substantially round and spherical particles have an alumina content of from about 41.5% to about 49% by weight.

In certain embodiments, the proppants have a bulk density of from about 1.35 g/cm^3 to about 1.55 g/cm^3. The term "bulk density", as used herein, refers to the weight per unit volume, including in the volume considered, the void spaces between the particles. In certain other embodiments, the proppants have a bulk density of from about 1.40 g/cm^3 to about 1.50 g/cm^3.

According to several exemplary embodiments, the proppants have any suitable permeability and fluid conductivity in accordance with ISO 13503-5: "Procedures for Measuring the Long-term Conductivity of Proppants," and expressed in terms of Darcy units, or Darcies (D). The proppants can have a long term permeability at 7,500 psi of at least about 1 D, at least about 2 D, at least about 5 D, at least about 10 D, at least about 20 D, at least about 40 D, at least about 80 D, at least about 120 D, or at least about 150 D. The proppants can have a long term permeability at 12,000 psi of at least about 1 D, at least about 2 D, at least about 3 D, at least about 4 D, at least about 5 D, at least about 10 D, at least about 25 D, or at least about 50 D. The proppants can have a long term conductivity at 7,500 psi of at least about 100 millidarcy-feet (mD-ft), at least about 200 mD-ft, at least about 300 mD-ft, at least about 500 mD-ft, at least about 1,000 mD-ft, at least about 1,500 mD-ft, at least about 2,000 mD-ft, or at least about 2,500 mD-ft. For example, the proppants can have a long term conductivity at 12,000 psi of at least about 50 mD-ft, at least about 100 mD-ft, at least about 200 mD-ft, at least about 300 mD-ft, at least about 500 mD-ft, at least about 1,000 mD-ft, or at least about 1,500 mD-ft.

In certain embodiments, the proppants have a crush strength at 10,000 psi of from about 5% to about 8.5%, and a long term fluid conductivity at 10,000 psi of from about 2500 mD-ft to about 3000 mD-ft. In certain other embodiments, the proppants have a crush strength at 10,000 psi of from about 5% to about 7.5%.

The proppants can have any suitable apparent specific gravity. In one or more exemplary embodiments, the proppants have an apparent specific gravity of less than 5, less than 4.5, less than 4.2, less than 4, less than 3.8, less than 3.5, or less than 3.2. In still other embodiments, the proppants have an apparent specific gravity of from about 2.50 to about 3.00, about 2.75 to about 3.25, about 2.8 to about 3.4, about 3.0 to about 3.5, or about 3.2 to about 3.8. The term "apparent specific gravity," (ASG) as used herein, refers to a number without units that is defined to be numerically equal to the weight in grams per cubic centimeter of volume, including void space or open porosity in determining the volume.

The proppants can have any suitable size. According to one or more exemplary embodiments, the proppants can have a size of at least about 100 mesh, at least about 80 mesh, at least about 60 mesh, at least about 50 mesh, or at least about 40 mesh. For example, the proppants can have a size from about 115 mesh to about 2 mesh, about 100 mesh to about 3 mesh, about 80 mesh to about 5 mesh, about 80 mesh to about 10 mesh, about 60 mesh to about 12 mesh, about 50 mesh to about 14 mesh, about 40 mesh to about 16 mesh, or about 35 mesh to about 18 mesh. In a particular embodiment, the proppants have a size of from about 20 to about 40 U.S. Mesh.

According to certain embodiments described herein, the proppants are made in a continuous process, while in other embodiments, the proppants are made in a batch process.

Suitable sintered, substantially round and spherical particles can also include proppants manufactured according to vibration-induced dripping methods, herein called "drip casting." Suitable drip casting methods and proppants made therefrom are disclosed in U.S. Pat. Nos. 8,865,631 and 8,883,693, U.S. Patent Application Publication No. 2012/0227968, and U.S. patent application Ser. No. 14/502,483, the entire disclosures of which are incorporated herein by reference. Proppants produced from the drip cast methods can have a specific gravity of at least about 2.5, at least about 2.7, at least about 3, at least about 3.3, or at least about 3.5. Proppants produced from the drip cast methods can have a specific gravity of less than 5, less than 4.5, or less than 4. The drip cast proppants can also have a surface roughness of less than 5 μm, less than 4 μm, less than 3 μm, less than 2.5 μm, less than 2 μm, less than 1.5 μm, or less than 1 μm. In one or more exemplary embodiments, the drip cast proppants have an average largest pore size of less than about 25 μm, less than about 20 μm, less than about 18 μm, less than about 16 μm, less than about 14 μm, or less than about 12 μm and/or a standard deviation in pore size of less than 6 μm, less than 4 μm, less than 3 μm, less than 2.5 μm, less than 2 μm, less than 1.5 μm, or less than 1 μm. In one or more exemplary embodiments, the drip cast proppants have less than 5,000, less than 4,500, less than 4,000, less than 3,500, less than 3,000, less than 2,500, or less than 2,200 visible pores at a magnification of 500× per square millimeter of proppant particulate.

The proppants, produced by the drip casting methods or the conventional methods, can have any suitable composition. The proppants can be or include silica and/or alumina in any suitable amounts. According to one or more embodiments, the proppants include less than 80 wt %, less than 60 wt %, less than 40 wt %, less than 30 wt %, less than 20 wt %, less than 10 wt %, or less than 5 wt % silica based on the total weight of the proppants. According to one or more embodiments, the proppants include from about 0.1 wt % to about 70 wt % silica, from about 1 wt % to about 60 wt % silica, from about 2.5 wt % to about 50 wt % silica, from

about 5 wt % to about 40 wt % silica, or from about 10 wt % to about 30 wt % silica. According to one or more embodiments, the proppants include at least about 30 wt %, at least about 50 wt %, at least about 60 wt %, at least about 70 wt %, at least about 80 wt %, at least about 90 wt %, or at least about 95 wt % alumina based on the total weight of the proppants. According to one or more embodiments, the proppants include from about 30 wt % to about 99.9 wt % alumina, from about 40 wt % to about 99 wt % alumina, from about 50 wt % to about 97 wt % alumina, from about 60 wt % to about 95 wt % alumina, or from about 70 wt % to about 90 wt % alumina. In one or more embodiments, the proppants produced by the processes disclosed herein can include alumina, bauxite, or kaolin, or any mixture thereof. For example, the proppants can be composed entirely of or composed essentially of alumina, bauxite, or kaolin, or any mixture thereof. The term "kaolin" is well known in the art and can include a raw material having an alumina content of at least about 40 wt % on a calcined basis and a silica content of at least about 40 wt % on a calcined basis. The term "bauxite" is well known in the art and can be or include a raw material having an alumina content of at least about 55 wt % on a calcined basis.

The electrically conductive material can be or include any suitable electrically conductive metal. For example, the metal can be or include iron, silver, gold, copper, aluminum, calcium, tungsten, zinc, nickel, lithium, platinum, palladium, rhodium, tin, carbon steel, or any combination or oxide thereof. The electrically conductive proppant can have an electrically conductive metal concentration of about 0.01 wt %, about 0.05 wt %, about 0.1 wt %, about 0.5 wt %, about 1 wt %, about 2 wt %, or about 5 wt % to about 6 wt %, about 8 wt %, about 10 wt %, about 12 wt %, or about 14 wt %. In one or more exemplary embodiments, the metals can include aluminum, copper and nickel and can be added to result in a proppant having a metal content of from about 5% to about 10% by weight.

The electrically conductive material can be or include any suitable electrically conductive polymer. Suitable conductive polymers include poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS), polyanilines (PANI), and polypyrroles (PPY) and can be added to result in a proppant having any suitable conductive polymer content, such as from about 0.1% to about 10% by weight. In one or more exemplary embodiments, the electrically conductive proppant can have a conductive polymer concentration of about 0.01 wt %, about 0.05 wt %, about 0.1 wt %, about 0.5 wt %, about 1 wt %, about 2 wt %, or about 5 wt % to about 6 wt %, about 8 wt %, about 10 wt %, about 12 wt %, or about 14 wt %. Suitable PEDOT:PSS, PANI and PYY conductive polymers are commercially available from Sigma-Aldrich. Certain specific embodiments of processes for coating proppant with a conductive polymer are described below in Example 2.

The electrically conductive material can be or include any suitable electrically conductive particle. Suitable conductive particles include graphite, single or double-walled carbon nanotubes, or other material that when present in the nanoscale particle size range exhibits sufficient electrical conductivity to allow for detection in the present invention. Suitable conductive particles can also include any suitable metal, such as iron, silver, gold, copper, aluminum, calcium, tungsten, zinc, nickel, lithium, platinum, tin, carbon steel, or any combination or oxide thereof. Such conductive particles can be added to result in an electrically conductive proppant having a conductive particle concentration of about 0.01 wt %, about 0.05 wt %, about 0.1 wt %, about 0.5 wt %, about

1 wt %, about 2 wt %, or about 5 wt % to about 6 wt %, about 8 wt %, about 10 wt %, about 12 wt %, or about 14 wt %. In one or more exemplary embodiments, the electrically conductive proppant can have a conductive nanoparticle content of from about 0.1% to about 10% by weight.

The conductive particles can have any suitable size. In one or more exemplary embodiments, the conductive particles have a size from about 1 nanometers (nm), about 5 nm, about 10 nm, about 50 nm, about 100 nm, about 500 nm, or about 1,000 to about 2,000 nm, about 5,000 nm, about 10,000 nm, about 15,000 nm, or about 20,000 nm in its largest dimension. For example, the conductive particles can be from about 2 nm to about 25,000 nm, about 25 nm to about 15,000 nm, about 50 nm to about 10,000 nm, about 150 nm to about 7,500, about 250 nm to about 4,000 nm, or about 750 nm to about 1,500 nm in its largest dimension. The conductive particles can also be from about 2 nm to about 2,000 nm, about 20 nm to about 500 nm, about 40 nm to about 300 nm, about 50 nm to about 250 nm, about 75 nm to about 200 nm, or about 100 nm to about 150 nm in its largest dimension.

In one or more exemplary embodiments of the present invention, the conductive particle is nano-sized or is a nanoparticle. In one or more exemplary embodiments, the conductive nanoparticle can have a size less than 500 nm, less than 250 nm, less than 150 nm, less than 100 nm, less than 95 nm, less than 90 nm, less than 85 nm, less than 80 nm, less than 75 nm, less than 70 nm, less than 65 nm, less than 60 nm, less than 55 nm, less than 50 nm, less than 45 nm, less than 40 nm, less than 35 nm, less than 30 nm, less than 25 nm, less than 20 nm, less than 15 nm, less than 10 nm, less than 5 nm, less than 2 nm, or less than 1 nm in its largest dimension.

In one or more exemplary embodiments, the electrically conductive material can be added to a ceramic proppant in its method of manufacture. Referring now to FIG. 1, an exemplary system for implementing a continuous process for preparing sintered, substantially round and spherical particles from a slurry is illustrated. The exemplary system illustrated in FIG. 1 is similar in configuration and operation to that described in U.S. Pat. No. 4,440,866, the entire disclosure of which is incorporated herein by reference. The operations performed by the exemplary system illustrated in FIG. 1 can also be used to make the particles according to a batch process, as described in Example 1 below.

In the system illustrated in FIG. 1, an alumina-containing raw material having an alumina content of from about 40% to about 55% by weight (on a calcined basis) is passed through a shredder 105 which slices and breaks apart the raw material into small chunks. In some embodiments, when the raw material as mined, or as received, (referred to herein as "untreated" raw material) is of such consistency that it can be processed as described herein without shredding, the shredder may be bypassed. Raw material fed through a shredder such as is illustrated in FIG. 1, is referred to as "treated" raw material.

In certain embodiments, the shredder breaks apart and slices the alumina-containing raw material so as to yield pieces having a diameter of less than about five inches, although pieces having smaller and larger diameters can be further processed into a slurry as described herein. Shredders and numerous other devices for slicing, chopping or comminuting the alumina-containing raw material, as well as commercial sources for same, such as the Gleason Foundry Company, are well known to those of ordinary skill in the art.

The treated or untreated alumina-containing raw material and water are fed to a blunger 110, which has a rotating blade that imparts a shear force to and further reduces the particle size of the raw material to form a slurry. In a continuous process, the raw material and water are continuously fed to the blunger. Blungers and similar devices for making slurries of such materials, as well as commercial sources for same are well known to those of ordinary skill in the art.

In certain embodiments, the electrically conductive material is added to the alumina-containing raw material and water in the blunger 110 to result in an electrically conductive material concentration of about 5% to about 10% by weight of the solids content in the slurry or just prior to the formation of pellets as described below. In one or more exemplary embodiments, the electrically conductive material added to the blunger 110 can be or include the conductive particles disclosed herein.

A sufficient amount of water is added to the blunger 110 to result in a slurry having a solids content in the range of from about 40% to about 60% by weight. In certain embodiments, a sufficient amount of water is added to the slurry such that the solids content of the slurry is from about 45% to about 55% by weight. In still other embodiments, a sufficient amount of water is added to the slurry such that the solids content of the slurry is about 50% by weight. The water added to the blunger 110 can be fresh water or deionized water. In a continuous process for preparing the slurry, the solids content of the slurry is periodically analyzed and the amount of water fed to the slurry adjusted to maintain the desired solids content. Methods for analyzing the solids content of a slurry and adjusting a feed of water are well known and understood by those of ordinary skill in the art.

In certain embodiments, a dispersant is added to the slurry in the blunger 110 to adjust the viscosity of the slurry to a target range as discussed further below. In other embodiments, the viscosity of the slurry in the blunger 110 is adjusted to the target range by the addition of a dispersant and a pH-adjusting reagent.

A dispersant may be added to the slurry prior to the addition of the electrically conductive material or other additives. In certain embodiments, the composition includes a dispersant in an amount of from about 0.15% to about 0.30% by weight based on the dry weight of the alumina-containing raw material.

Exemplary materials suitable for use as a dispersant in the compositions and methods described herein include but are not limited to sodium polyacrylate, ammonium polyacrylate, ammonium polymethacrylate, tetra sodium pyrophosphate, tetra potassium pyrophosphate, polyphosphate, ammonium polyphosphate, ammonium citrate, ferric ammonium citrate, and polyelectrolytes such as a composition of ammonium polymethacrylate and water commercially available from a variety of sources, such as, Kemira Chemicals under the trade name C-211, Phoenix Chemicals, Bulk Chemical Systems under the trade name BCS 4020 and R.T. Vanderbilt Company, Inc. under the trade name DARVAN C. Generally, the dispersant can be any material that will adjust the viscosity of the slurry to a target viscosity such that the slurry can be subsequently processed through one or more pressure nozzles of a fluidizer. In certain embodiments, the target viscosity is less than 150 centipoises (cps) (as determined on a Brookfield Viscometer with a #61 spindle). In other embodiments, the target viscosity is less than 100 cps.

According to embodiments in which a pH-adjusting reagent is used, a sufficient amount of a pH-adjusting

reagent is added to the slurry to adjust the pH of the slurry to a range of from about 8 to about 11. In certain embodiments, a sufficient amount of the pH-adjusting reagent is added to the slurry to adjust the pH to about 9, about 9.5, about 10 or about 10.5. The pH of the slurry can be periodically analyzed by a pH meter, and the amount of pH-adjusting reagent fed to the slurry adjusted to maintain a desired pH. Methods for analyzing the pH of a slurry and adjusting the feed of the pH-adjusting reagent are within the ability of those of ordinary skill in the art. Exemplary materials suitable for use as a pH-adjusting reagent in the compositions and methods described herein include but are not limited to ammonia and sodium carbonate.

Generally, the target viscosity of the compositions is a viscosity that can be processed through a given type and size of pressure nozzle in a fluidizer, without becoming clogged. Generally, the lower the viscosity of the slurry, the more easily it can be processed through a given fluidizer. However, the addition of too much dispersant can cause the viscosity of the slurry to increase to a point that it cannot be satisfactorily processed through a given fluidizer. One of ordinary skill in the art can determine the target viscosity for given fluidizer types through routine experimentation.

The blunger 110 mixes the alumina-containing raw material, electrically conductive material, water, dispersant and pH-adjusting reagent until a slurry is formed. The length of time required to form a slurry is dependent on factors such as the size of the blunger, the speed at which the blunger is operating, and the amount of material in the blunger.

From the blunger 110, the slurry is fed to a tank 115, where the slurry is continuously stirred, and a binder is added in an amount of from about 0.2% to about 5.0% by weight, based on the total dry weight of the alumina-containing raw material and the electrically conductive material. In certain embodiments, the binder is added in an amount of from about 0.2% to about 3.0% by weight based on the total dry weight of the alumina-containing raw material and the electrically conductive material. Suitable binders include but are not limited to polyvinyl acetate, polyvinyl alcohol (PVA), methylcellulose, dextrin and molasses. In certain embodiments, the binder is PVA having a molecular weight of from about 20,000 to 100,000 Mn. "Mn" represents the number average molecular weight which is the total weight of the polymeric molecules in a sample, divided by the total number of polymeric molecules in that sample.

The tank 115 maintains the slurry created by the blunger 110. However, the tank 115 stirs the slurry with less agitation than the blunger, so as to mix the binder with the slurry without causing excessive foaming of the slurry or increasing the viscosity of the slurry to an extent that would prevent the slurry from being fed through the pressurized nozzles of a fluidizer.

In another embodiment, the binder can be added to the slurry while in the blunger. In this embodiment, the blunger optionally has variable speeds, including a high speed to achieve the high intensity mixing for breaking down the raw material into a slurry form, and a low speed to mix the binder with the slurry without causing the above-mentioned excessive foaming or increase in viscosity.

Referring again to the tank 115 illustrated in FIG. 1, the slurry is stirred in the tank, after addition of the binder, for a time sufficient to thoroughly mix the binder with the slurry. In certain embodiments, the slurry is stirred in the tank for up to about 30 minutes following the addition of binder. In other embodiments, the slurry is stirred in the tank 115 for

at least about 30 minutes. In still other embodiments, the slurry is stirred in the tank for more than about 30 minutes after addition of the binder.

Tank **115** can also be a tank system comprised of one, two, three or more tanks. Any configuration or number of tanks that enables the thorough mixing of the binder with the slurry is sufficient. In a continuous process, water, and one or more of dust, oversize particles, or undersize particles from a subsequent fluidizer or other apparatus can be added to the slurry in the tank **115**.

From the tank **115**, the slurry is fed to a heat exchanger **120**, which heats the slurry to a temperature of from about 25° C. to about 90° C. From the heat exchanger **120**, the slurry is fed to a pump system **125**, which feeds the slurry, under pressure, to a fluidizer **130**.

A grinding mill(s) and/or a screening system(s) (not illustrated) can be inserted at one or more places in the system illustrated in FIG. **1** prior to feeding the slurry to the fluidizer to assist in breaking any larger-sized alumina-containing raw material down to a target size suitable for feeding to the fluidizer. In certain embodiments, the target size is less than 230 mesh. In other embodiments, the target size is less than 325 mesh, less than 270 mesh, less than 200 mesh or less than 170 mesh. The target size is influenced by the ability of the type and/or size of the pressure nozzle in the subsequent fluidizer to atomize the slurry without becoming clogged.

If a grinding system is employed, it is charged with a grinding media suitable to assist in breaking the raw material down to a target size suitable for subsequent feeding through one or more pressure nozzles of a fluidizer. If a screening system is employed, the screening system is designed to remove particles larger than the target size from the slurry. For example, the screening system can include one or more screens, which are selected and positioned so as to screen the slurry to particles that are smaller than the target size.

Referring again to FIG. **1**, fluidizer **130** is of conventional design, such as described in, for example, U.S. Pat. No. 3,533,829 and U.K. Patent No. 1,401,303. Fluidizer **130** includes at least one atomizing nozzle **132** (three atomizing nozzles **132** being shown in FIG. **1**), which is a pressure nozzle of conventional design. In other embodiments, one or more two-fluid nozzles are suitable. The design of such nozzles is well known, for example from K. Masters: "Spray Drying Handbook", John Wiley and Sons, New York (1979).

Fluidizer **130** further includes a particle bed **134**, which is supported by a plate **136**, such as a perforated, straight or directional plate. Hot air flows through the plate **136**. The particle bed **134** comprises seeds from which green pellets of a target size can be grown. The term "green pellets" and related forms, as used herein, refers to substantially round and spherical particles which have been formed from the slurry but are not sintered. When a perforated or straight plate is used, the seeds also serve to obtain plug flow in the fluidizer. Plug flow is a term known to those of ordinary skill in the art, and can generally be described as a flow pattern where very little back mixing occurs. The seed particles are smaller than the target size for green pellets made according to the present methods. In certain embodiments, the seed comprises from about 5% to about 20% of the total volume of a green pellet formed therefrom. Slurry is sprayed, under pressure, through the atomizing nozzles **132**, and the slurry spray coats the seeds to form green pellets that are substantially round and spherical.

External seeds can be placed on the perforated plate **136** before atomization of the slurry by the fluidizer begins. If external seeds are used, the seeds can be prepared in a slurry

process similar to that illustrated in FIG. **1**, where the seeds are simply taken from the fluidizer at a target seed size. External seeds can also be prepared in a high intensity mixing process such as that described in U.S. Pat. No. 4,879,181, the entire disclosure of which is hereby incorporated by reference.

According to certain embodiments, external seeds are made from either a raw material having at least the same alumina content as the raw material used to make the slurry, or from a raw material having more or less alumina than the raw material used to make the slurry. In certain embodiments, the slurry has an alumina content that is at least 10%, at least 20%, or at least 30% less than that of the seeds. In other embodiments, the external seeds have an alumina content less than that of the slurry, such as at least 10%, at least 20%, or at least 30% less than that of the slurry.

Alternatively, seeds for the particle bed are formed by the atomization of the slurry, thereby providing a method by which the slurry "self-germinates" with its own seed. According to one such embodiment, the slurry is fed through the fluidizer **130** in the absence of a seeded particle bed **134**. The slurry droplets exiting the nozzles **132** solidify, but are small enough initially that they get carried out of the fluidizer **130** by air flow and caught as "dust" (fine particles) by a dust collector **145**, which may, for instance, be an electrostatic precipitator, a cyclone, a bag filter, a wet scrubber or a combination thereof. The dust from the dust collector is then fed to the particle bed **134** through dust inlet **162**, where it is sprayed with slurry exiting the nozzles **132**. The dust may be recycled a sufficient number of times, until it has grown to a point where it is too large to be carried out by the air flow and can serve as seed. The dust can also be recycled to another operation in the process, for example, the tank **115**.

Referring again to FIG. **1**, hot air is introduced to the fluidizer **130** by means of a fan and an air heater, which are schematically represented at **138**. The velocity of the hot air passing through the particle bed **134** is from about 0.9 meters/second to about 1.5 meters/second, and the depth of the particle bed **134** is from about 2 centimeters to about 60 centimeters. The temperature of the hot air when introduced to the fluidizer **130** is from about 250° C. to about 650° C. The temperature of the hot air as it exits from the fluidizer **130** is less than about 250° C., and in some embodiments is less than about 100° C.

The distance between the atomizing nozzles **132** and the plate **136** is optimized to avoid the formation of dust which occurs when the nozzles **132** are too far away from the plate **126** and the formation of irregular, coarse particles which occurs when the nozzles **132** are too close to the plate **136**. The position of the nozzles **132** with respect to the plate **136** is adjusted on the basis of an analysis of powder sampled from the fluidizer **130**.

The green pellets formed by the fluidizer accumulate in the particle bed **134**. In a continuous process, the green pellets formed by the fluidizer **130** are withdrawn through an outlet **140** in response to the level of product in the particle bed **134** in the fluidizer **130**, so as to maintain a given depth in the particle bed. A rotary valve **150** conducts green pellets withdrawn from the fluidizer **130** to an elevator **155**, which feeds the green pellets to a screening system **160**, where the green pellets are separated into one or more fractions, for example, an oversize fraction, a product fraction, and an undersize fraction.

The oversize fraction exiting the screening unit **160** includes those green pellets that are larger than the desired product size. In a continuous process, the oversize green

pellets may be recycled to tank **115**, where at least some of the oversize green pellets can be broken down and blended with slurry in the tank. Alternatively, oversize green pellets can be broken down and recycled to the particle bed **134** in the fluidizer **130**. The undersize fraction exiting the screening system **160** includes those green pellets that are smaller than the desired product size. In a continuous process, these green pellets may be recycled to the fluidizer **130**, where they can be fed through an inlet **162** as seeds or as a secondary feed to the fluidizer **130**.

The product fraction exiting the screening system **160** includes those green pellets having the desired product size. These green pellets are sent to a pre-sintering device **165**, for example, a calciner, where the green pellets are dried or calcined prior to sintering. In certain embodiments, the green pellets are dried to a moisture content of less than about 18% by weight, or less than about 15% by weight, about 12% by weight, about 10% by weight, about 5% by weight, or about 1% by weight.

After drying and/or calcining, the green pellets are fed to a sintering device **170**, in which the green pellets are sintered for a period of time sufficient to enable recovery of sintered, substantially round and spherical particles having one or more of a desired apparent specific gravity, bulk density, and crush strength. Alternatively, the pre-sintering device **165** can eliminated if the sintering device **170** can provide sufficient calcining and/or drying conditions (i.e., drying times and temperatures that dry the green pellets to a target moisture content prior to sintering), followed by sufficient sintering conditions.

The specific time and temperature to be employed for sintering is dependent on the starting ingredients and the desired density for the sintered particles. In some embodiments, sintering device **170** is a rotary kiln, operating at a temperature of from about 1000° C. to about 1600° C., for a period of time from about 5 to about 90 minutes. In certain embodiments, a rotary kiln is operated at a temperature of about 1000° C., about 1200° C., about 1300° C., about 1400° C. or about 1500° C. In certain embodiments, the green pellets have a residence time in the sintering device of from about 50 minutes to about 70 minutes, or from about 30 minutes to about 45 minutes. After the particles exit the sintering device **170**, they can be further screened for size, and tested for quality control purposes. Inert atmosphere sintering can be used to limit or prevent the oxidation of the electrically conductive material. Techniques for replacing the oxygen rich atmosphere in the sintering device with an inert gas such as argon, nitrogen, or helium are well known to those of ordinary skill in the art. Generally, oxygen is replaced with an inert gas such that 0.005% oxygen or less remains in the sintering atmosphere.

In one or more exemplary embodiments, the ceramic proppant can be manufactured in a manner that creates porosity in the proppant grain. A process to manufacture a suitable porous ceramic proppant is described in U.S. Pat. No. 7,036,591, the entire disclosure of which is incorporated herein by reference. In this case the electrically conductive material can be impregnated into the pores of the proppant grains to a concentration of about 0.01 wt %, about 0.05 wt %, about 0.1 wt %, about 0.5 wt %, about 1 wt %, about 2 wt %, or about 5 wt % to about 6 wt %, about 8 wt %, about 10 wt %, about 12 wt %, about 15 wt %, or about 20 wt % based on the weight of the electrically conductive proppant. Water soluble coatings such as polylactic acid can be used to coat these particles to allow for delayed/timed release of conductive particles.

The ceramic proppants can have any suitable porosity. The ceramic proppants can include an internal interconnected porosity from about 1%, about 2%, about 4%, about 6%, about 8%, about 10%, about 12%, or about 14% to about 18%, about 20%, about 22%, about 24%, about 26%, about 28%, about 30%, about 34%, about 38%, or about 45% or more. In several exemplary embodiments, the internal interconnected porosity of the ceramic proppants is from about 5 to about 35%, about 5 to about 15%, or about 15 to about 35%. According to several exemplary embodiments, the ceramic proppants have any suitable average pore size. For example, the ceramic proppant can have an average pore size from about 2 nm, about 10 nm, about 15 nm, about 55 nm, about 110 nm, about 520 nm, or about 1,100 nm to about 2,200 nm, about 5,500 nm, about 11,000 nm, about 17,000 nm, or about 25,000 nm or more in its largest dimension. For example, the ceramic proppant can have an average pore size from about 3 nm to about 30,000 nm, about 30 nm to about 18,000 nm, about 200 nm to about 9,000 nm, about 350 nm to about 4,500 nm, or about 850 nm to about 1,800 nm in its largest dimension.

According to several exemplary embodiments, the proppants disclosed herein are coated with a resin material. According to several exemplary embodiments, at least about 50%, at least about 75%, at least about 85%, at least about 90%, at least about 95%, or least about 99% of the proppants are coated with the resin material. In one or more exemplary embodiments, one or more of the electrically conductive proppant particulates in a proppant pack are coated with the resin material. In one or more exemplary embodiments, all of the electrically conductive proppant particulates in a proppant pack are coated with the resin material. In one or more exemplary embodiments, all of the proppants in a proppant pack are coated with the resin material. In one or more exemplary embodiments, all of any non-electrically conductive proppant particulates, or those proppant particulates not containing the electrically conductive material, in a proppant pack are coated with the resin material while the electrically conductive proppant particulates are uncoated. In one or more exemplary embodiments, the electrically conductive proppant particulates in a proppant pack are coated with the resin material while the non-electrically conductive proppant particulates are uncoated.

According to several exemplary embodiments, at least a portion of the surface area of each of the coated proppant particulates is covered with the resin material. According to several exemplary embodiments, at least about 10%, at least about 25%, at least about 50%, at least about 75%, at least about 90%, at least about 95%, or at least about 99% of the surface area of the coated proppant particulates is covered with the resin material. According to several exemplary embodiments, about 40% to about 99.9%, about 85% to about 99.99%, or about 98% to about 100% of the surface area of the coated proppant particulates is covered with the resin material. According to several exemplary embodiments, the entire surface area of the coated proppant particulates is covered with the resin material. For example, the coated proppant particulates can be encapsulated with the resin material.

According to several exemplary embodiments, the resin material is present on the resin coated proppant particulates in any suitable amount. According to several exemplary embodiments, the resin coated proppant particulates contain at least about 0.1 wt % resin, at least about 0.5 wt % resin, at least about 1 wt % resin, at least about 2 wt % resin, at least about 4 wt % resin, at least about 6 wt % resin, at least about 10 wt % resin, or at least about 20 wt % resin, based

on the total weight of the resin coated proppant particulates. According to several exemplary embodiments, the resin coated proppant particulates contain about 0.01 wt %, about 0.2 wt %, about 0.8 wt %, about 1.5 wt %, about 2.5 wt %, about 3.5 wt %, or about 5 wt % to about 8 wt %, about 15 wt %, about 30 wt %, about 50 wt %, or about 80 wt % resin, based on the total weight of the resin coated proppant particulates.

According to several exemplary embodiments, the resin material includes any suitable resin. For example, the resin material can include a phenolic resin, such as a phenol-formaldehyde resin. According to several exemplary embodiments, the phenol-formaldehyde resin has a molar ratio of formaldehyde to phenol (F:P) from a low of about 0.6:1, about 0.9:1, or about 1.2:1 to a high of about 1.9:1, about 2.1:1, about 2.3:1, or about 2.8:1. For example, the phenol-formaldehyde resin can have a molar ratio of form-aldehyde to phenol of about 0.7:1 to about 2.7:1, about 0.8:1 to about 2.5:1, about 1:1 to about 2.4:1, about 1.1:1 to about 2.6:1, or about 1.3:1 to about 2:1. The phenol-formaldehyde resin can also have a molar ratio of formaldehyde to phenol of about 0.8:1 to about 0.9:1, about 0.9:1 to about 1:1, about 1:1 to about 1.1:1, about 1.1:1 to about 1.2:1, about 1.2:1 to about 1.3:1, or about 1.3:1 to about 1.4:1.

According to several exemplary embodiments, the phe-nol-formaldehyde resin has a molar ratio of less than 1:1, less than 0.9:1, less than 0.8:1, less than 0.7:1, less than 0.6:1, or less than 0.5:1. For example, the phenol-formal-dehyde resin can be or include a phenolic novolac resin. Phenolic novolac resins are well known to those of ordinary skill in the art, for instance see U.S. Pat. No. 2,675,335 to Rankin, U.S. Pat. No. 4,179,429 to Hanauye, U.S. Pat. No. 5,218,038 to Johnson, and U.S. Pat. No. 8,399,597 to Pullichola, the entire disclosures of which are incorporated herein by reference. Suitable examples of commercially available novolac resins include novolac resins available from Plenco™, Durite® resins available from Momentive, and novolac resins available from S.I. Group.

According to several exemplary embodiments, the phe-nol-formaldehyde resin has a weight average molecular weight from a low of about 200, about 300, or about 400 to a high of about 1,000, about 2,000, or about 6,000. For example, the phenol-formaldehyde resin can have a weight average molecular weight from about 250 to about 450, about 450 to about 550, about 550 to about 950, about 950 to about 1,500, about 1,500 to about 3,500, or about 3,500 to about 6,000. The phenol-formaldehyde resin can also have a weight average molecular weight of about 175 to about 800, about 700 to about 3,330, about 1,100 to about 4,200, about 230 to about 550, about 425 to about 875, or about 2,750 to about 4,500.

According to several exemplary embodiments, the phe-nol-formaldehyde resin has a number average molecular weight from a low of about 200, about 300, or about 400 to a high of about 1,000, about 2,000, or about 6,000. For example, the phenol-formaldehyde resin can have a number average molecular weight from about 250 to about 450, about 450 to about 550, about 550 to about 950, about 950 to about 1,500, about 1,500 to about 3,500, or about 3,500 to about 6,000. The phenol-formaldehyde resin can also have a number average molecular weight of about 175 to about 800, about 700 to about 3,000, about 1,100 to about 2,200, about 230 to about 550, about 425 to about 875, or about 2,000 to about 2,750.

According to several exemplary embodiments, the phe-nol-formaldehyde resin has a z-average molecular weight from a low of about 200, about 300, or about 400 to a high

of about 1,000, about 2,000, or about 9,000. For example, the phenol-formaldehyde resin can have a z-average molecular weight from about 250 to about 450, about 450 to about 550, about 550 to about 950, about 950 to about 1,500, about 1,500 to about 3,500, about 3,500 to about 6,500, or about 6,500 to about 9,000. The phenol-formaldehyde resin can also have a z-average molecular weight of about 175 to about 800, about 700 to about 3,330, about 1,100 to about 4,200, about 230 to about 550, about 425 to about 875, or about 4,750 to about 8,500.

According to several exemplary embodiments, the phe-nol-formaldehyde resin has a polydispersity index from a low of about 1, about 1.75, or about 2.5 to a high of about 2.75, about 3.5, or about 4.5. For example, the phenol-formaldehyde resin can have a polydispersity index from about 1 to about 1.75, about 1.75 to about 2.5, about 2.5 to about 2.75, about 2.75 to about 3.25, about 3.25 to about 3.75, or about 3.75 to about 4.5. The phenol-formaldehyde resin can also have a polydispersity index of about 1 to about 1.5, about 1.5 to about 2.5, about 2.5 to about 3, about 3 to about 3.35, about 3.35 to about 3.9, or about 3.9 to about 4.5.

According to several exemplary embodiments, the phe-nol-formaldehyde resin has any suitable viscosity. The phe-nol-formaldehyde resin can be a solid or liquid at 25° C. For example, the viscosity of the phenol-formaldehyde resin can be from about 1 centipoise (cP), about 100 cP, about 250 cP, about 500 cP, or about 700 cP to about 1,000 cP, about 1,250 cP, about 1,500 cP, about 2,000 cP, or about 2,200 cP at a temperature of about 25° C. In another example, the phenol-formaldehyde resin can have a viscosity from about 1 cP to about 125 cP, about 125 cP to about 275 cP, about 275 cP to about 525 cP, about 525 cP to about 725 cP, about 725 cP to about 1,100 cP, about 1,100 cP to about 1,600 cP, about 1,600 cP to about 1,900 cP, or about 1,900 cP to about 2,200 cP at a temperature of about 25° C. In another example, the phenol-formaldehyde resin can have a viscosity from about 1 cP to about 45 cP, about 45 cP to about 125, about 125 cP to about 550 cP, about 550 cP to about 825 cP, about 825 cP to about 1,100 cP, about 1,100 cP to about 1,600 cP, or about 1,600 cP to about 2,200 cP at a temperature of about 25° C. The viscosity of the phenol-formaldehyde resin can also be from about 500 cP, about 1,000 cP, about 2,500 cP, about 5,000 cP, or about 7,500 cP to about 10,000 cP, about 15,000 cP, about 20,000 cP, about 30,000 cP, or about 75,000 cP at a temperature of about 150° C. For example, the phenol-formaldehyde resin can have a viscosity from about 750 cP to about 60,000 cP, about 1,000 cP to about 35,000 cP, about 4,000 cP to about 25,000 cP, about 8,000 cP to about 16,000 cP, or about 10,000 cP to about 12,000 cP at a temperature of about 150° C. The viscosity of the phenol-formaldehyde resin can be determined using a Brookfield viscometer.

According to several exemplary embodiments, the phe-nol-formaldehyde resin can have pH from a low of about 1, about 2, about 3, about 4, about 5, about 6, about 7 to a high of about 8, about 9, about 10, about 11, about 12, or about 13. For example, the phenol-formaldehyde resin can have a pH from about 1 to about 2.5, about 2.5 to about 3.5, about 3.5 to about 4.5, about 4.5 to about 5.5, about 5.5 to about 6.5, about 6.5 to about 7.5, about 7.5 to about 8.5, about 8.5 to about 9.5, about 9.5 to about 10.5, about 10.5 to about 11.5, about 11.5 to about 12.5, or about 12.5 to about 13.

According to several exemplary embodiments of the present invention, the resin coating applied to the proppant particulates is an epoxy resin. According to such embodi-ments, the resin coating can include any suitable epoxy resin. For example, the epoxy resin can include bisphenol A, bisphenol F, aliphatic, or glycidylamine epoxy resins, and

any mixtures or combinations thereof. An example of a commercially available epoxy resin is BE188 Epoxy Resin, available from Chang Chun Plastics Co., Ltd.

According to several exemplary embodiments, the epoxy resin can have any suitable viscosity. The epoxy resin can be a solid or liquid at 25° C. For example, the viscosity of the epoxy resin can be from about 1 cP, about 100 cP, about 250 cP, about 500 cP, or about 700 cP to about 1,000 cP, about 1,250 cP, about 1,500 cP, about 2,000 cP, or about 2,200 cP at a temperature of about 25° C. In another example, the epoxy resin can have a viscosity from about 1 cP to about 125 cP, about 125 cP to about 275 cP, about 275 cP to about 525 cP, about 525 cP to about 725 cP, about 725 cP to about 1,100 cP, about 1,100 cP to about 1,600 cP, about 1,600 cP to about 1,900 cP, or about 1,900 cP to about 2,200 cP at a temperature of about 25° C. In another example, the epoxy resin can have a viscosity from about 1 cP to about 45 cP, about 45 cP to about 125 cP, about 125 cP to about 550 cP, about 550 cP to about 825 cP, about 825 cP to about 1,100 cP, about 1,100 cP to about 1,600 cP, or about 1,600 cP to about 2,200 cP at a temperature of about 25° C. The viscosity of the epoxy resin can also be from about 500 cP, about 1,000 cP, about 2,500 cP, about 5,000 cP, or about 7,000 cP to about 10,000 cP, about 12,500 cP, about 15,000 cP, about 17,000 cP, or about 20,000 cP at a temperature of about 25° C. In another example, the epoxy resin can have a viscosity from about 1,000 cP to about 12,000 cP, about 2,000 cP to about 11,000 cP, about 4,000 cP to about 10,500 cP, or about 7,500 cP to about 9,500 cP at a temperature of about 25° C. The viscosity of the epoxy resin can also be from about 500 cP, about 1,000 cP, about 2,500 cP, about 5,000 cP, or about 7,500 cP to about 10,000 cP, about 15,000 cP, about 20,000 cP, about 30,000 cP, or about 75,000 cP at a temperature of about 150° C. For example, the epoxy resin can have a viscosity from about 750 cP to about 60,000 cP, about 1,000 cP to about 35,000 cP, about 4,000 cP to about 25,000 cP, about 8,000 cP to about 16,000 cP, or about 10,000 cP to about 12,000 cP at a temperature of about 150° C.

According to several exemplary embodiments, the epoxy resin can have pH from a low of about 1, about 2, about 3, about 4, about 5, about 6, about 7 to a high of about 8, about 9, about 10, about 11, about 12, or about 13. For example, the epoxy resin can have a pH from about 1 to about 2.5, about 2.5 to about 3.5, about 3.5 to about 4.5, about 4.5 to about 5.5, about 5.5 to about 6.5, about 6.5 to about 7.5, about 7.5 to about 8.5, about 8.5 to about 9.5, about 9.5 to about 10.5, about 10.5 to about 11.5, about 11.5 to about 12.5, or about 12.5 to about 13.

Methods for coating proppant particulates with resins are well known to those of ordinary skill in the art, for instance see U.S. Pat. No. 2,378,817 to Wrightsman, U.S. Pat. No. 4,873,145 to Okada and U.S. Pat. No. 4,888,240 to Graham, the entire disclosures of which are incorporated herein by reference.

According to several exemplary embodiments of the present invention, a curing agent is applied to the resin-coated proppant particulates in order to accelerate the transition of the resin from a liquid to a solid state. Suitable curing agents include curing agents that will leave active amine or epoxy sites on the surface of the resin coating. Suitable curing agents will depend on the specific resin chemistry employed and can include amines, acids, acid anhydrides, and epoxies. In several exemplary embodiments of the present invention, a phenolic resin material is applied to the surface of the proppant particulates and cured with an amine curing agent in order to leave active amine sites on the

resin coated surface of the proppant particulates. In several exemplary embodiments, the phenolic resin is cured with hexamethylenetetramine, also known as hexamine. An example of a commercially available hexamine is Hexion™; which is available from Momentive.

In one or more exemplary embodiments, the conductive particles are treated and/or coated with one or more chemicals or ligands to impart surface functionality to the conductive particles. These coatings can be selected from organic compound containing materials and/or organic compounds of varying chain lengths, each having functional groups on the terminus of their respective chains to modify or tailor the solubility (solubility, as used herein, also refers to a suspension or slurry) of the conductive particles in a produced fluid. These coatings can also be selected from organic compound containing materials and/or organic compounds of varying chain lengths, each having functional groups on the terminus of their respective chains to modify a surface functionality of the conductive particles so that they have an affinity for an outer surface of the proppant material in a proppant pack. These coatings can also be selected from organic compound containing materials and/or organic compounds of varying chain lengths, each having functional groups on the terminus of their respective chains to modify a surface functionality of the conductive particles so that they have an affinity for a resin coating of the resin coated proppant. Many commercially available surfactants can be used for these purposes. Ligands that are multifunctional can also be used as a coating, with one end of the ligand molecule binding to the conductive particle and the other end of the ligand molecule affecting the dispersibility of the conductive particle throughout a proppant pack. These multi-functional ligands can be modified by traditional organic synthetic methods and principles to increase or decrease the affinity of the conductive particles to the outer surfaces of the proppants in the proppant pack. Examples of the types of functional groups that can be used are carboxylates, amines, thiols, polysiloxanes, silanes, alcohols, and other species capable of binding to the conductive particle or the proppant surface.

The conductive particles can be infused into the pores of the proppant in any suitable manner, with or without the use of a solvent. Methods for infusing a porous proppant particulate are well known to those of ordinary skill in the art, for instance see U.S. Pat. Nos. 5,964,291 and 7,598,209, and similar processes such as vacuum infusion, thermal infusion, capillary action, ribbon blending at room or elevated temperature, microwave blending or pug mill processing can be utilized to infuse porous proppant particulates with one or more conductive particles according to several exemplary embodiments of the present invention. For example, the conductive particles can be infused into a porous proppant using a thermal infusion process whereby the porous proppant is heated and wetted with a solution containing the conductive particle. As the porous proppant cools, capillary action causes the conductive particles to infuse into the porous proppant.

It has been found that infusing the conductive particles into pores of the proppant particulates can encourage the conductive particles to stay on the surface of the proppant particulates once the proppant particulates placed into one or more subterranean fractures. Once the conductive particles have eluted from the pores, most of the conductive particles should remain at or near the proppant surface(s) of the proppant pack because the conductive particles have a greater affinity for the resin coat on the proppant particulates

and/or outer surfaces of the proppant particulates than for fracturing fluid(s) and/or produced fluid(s).

In several exemplary embodiments, separation of the conductive particles from the electrically conductive proppant can be accomplished by the conductive particles leaching, eluting, diffusing, bleeding, discharging, draining, seeping, or leaking out of the porous proppant and/or the coated proppant, or any combination thereof. Further, this leaching, eluting, diffusing, bleeding, discharging, draining, seeping, or leaking out of the porous proppant and/or the coated proppant, or any combination thereof can be further controlled by a permeable, semi-permeable, and/or degradable coating. According to certain embodiments, the degradable coating can include one or more of water-soluble polymers and cross-linkable water-soluble polymers. Suitable water-soluble polymers and cross-linkable water-soluble polymers are disclosed in U.S. Pat. No. 6,279,656, the entire disclosure of which is incorporated herein by reference. According to several exemplary embodiments in which the degradable coating includes one or more of water-soluble polymers and cross-linkable water-soluble polymers, the solubility parameters of such polymers can be controlled to adjust the timing of the solubility or degradation of the coating. Such parameters can include molecular weight, the hydrophilic/lipophilic balance of the polymers, and the extent of cross-linking of the polymers. According to several exemplary embodiments, the degradable coating includes a degradable polymer such as polylactic acid, cellulose acetate, methyl cellulose or combinations thereof and will degrade inside the hydraulic fracture to allow for the release of the conductive particles at different time intervals.

In one or more exemplary embodiments, the phenol-formaledehyde resins and/or epoxy resins are semi-permeable such that the conductive particles can leach, elute, diffuse, bleed, discharge, desorb, dissolve, drain, seep, or leak from the coated proppant particulates at any suitable rate. According to one or more exemplary embodiments, the conductive particles can leach, elute, diffuse, bleed, discharge, desorb, dissolve, drain, seep, or leak from the coated proppant particulates at a rate of at least about 0.1 parts-per-million per gram of proppant particulates per day (expressed herein as ppm/(gram*day)), at least about 0.5 ppm/(gram*day), at least about 1 ppm/(gram*day), at least about 1.5 ppm/(gram*day), at least about 2 ppm/(gram*day), at least about 3 ppm/(gram*day), at least about 5 ppm/(gram*day), at least about 7 ppm/(gram*day), or at least about 10 ppm/(gram*day) for at least about 2 months, at least about 6 months, at least about 9 months, at least about 1 year, or at least about 2 years. For example, the conductive particles can elute from the coated proppant particulates at a rate from about 0.01 ppm/(gram*day), about 0.075 ppm/(gram*day), about 0.1 ppm/(gram*day), about 0.25 ppm/(gram*day), about 0.75 ppm/(gram*day), about 1.5 ppm/(gram*day), about 2.25 ppm/(gram*day), or about 3 ppm/(gram*day) to about 4 ppm/(gram*day), about 5 ppm/(gram*day), about 6 ppm/(gram*day), about 7 ppm/(gram*day), about 8 ppm/(gram*day), about 9 ppm/(gram*day), about 10 ppm/(gram*day), about 20 ppm/(gram*day), about 30 ppm/(gram*day), or about 50 ppm/(gram*day) for at least about 2 months, at least about 6 months, at least about 9 months, at least about 1 year, or at least about 2 years.

In one or more exemplary embodiments, the conductive particles are mixed with an activator that can react with the resin coating to provide an activator mixture that can be infused into pores of the proppant. As described herein, the term "activator" means a chemical or composition that causes a crosslinking reaction of the resin coating.

The activator can be or include any one or more suitable liquid epoxy resins and solid epoxy resins. Examples of suitable liquid epoxy resins are D.E.R.™ 317, D.E.R. 321, D.E.R. 331, D.E.R. 332, D.E.R. 351, D.E.R. 354, D.E.R. 3913, D.E.R. 732 and D.E.R. 736, which are commercially available from Dow Chemical. Examples of an water dispersible liquid epoxy is D.E.R. 383 and XY 92589.00, which is available from Dow Chemical, and EPOTUF 38-690, which is available from Reichhold Inc. Examples of commercially available water dispersible solid epoxy resins include Ancarez® AR462 Resin and Ancarez® AR555 Epoxy Resin, which are available from Air Products and Chemicals, Inc. and D.E.R.™ 671, D.E.R.™ 916 Epoxy Resins, which is available from Dow Chemical. In one or more exemplary embodiments, the activator can be or include any combination of D.E.R. 3913, D.E.R. 732, and/or D.E.R. 736. According to several exemplary embodiments, suitable activators for epoxy resins cured with an epoxy coating that leaves active epoxy sites on the resin coated surface of the proppant particulate include water dispersible amine-rich resins. Examples of commercially available water dispersible amine-rich resin activators include Anquamine® 701 and Anquawhite™ 100, which are both available from Air Products and Chemicals, Inc., and EPOTUF 37-685, EPOTUF 37-667, and EPOTUF37-680 available from Reichhold Inc.

The activator mixture can be infused into porous proppant with or without the use of a solvent. As disclosed herein, processes such as vacuum infusion, thermal infusion, capillary action, ribbon blending at room or elevated temperature, microwave blending or pug mill processing can be utilized to infuse porous proppant particulates with an activator mixture according to several exemplary embodiments of the present invention. It has been found that infusing the activator mixture into pores of the proppant particulates to provide electrically conductive proppant can encourage the activator to migrate to and stay on the surfaces of the electrically conductive proppant particulates. In one or more exemplary embodiments, once the activator has eluted from the pores, most of the activator should remain at or near the electrically conductive proppant surface(s) because the activator has a greater affinity for the resin coat of the electrically conductive proppant particulates than for the surrounding fluids. This can cause the conductive particles mixed with the activator to likewise elute from the pores and reside at or near the electrically conductive proppant surface(s).

In one or more exemplary embodiments, the phenol-formaledehyde resins and/or epoxy resins are semi-permeable such that the activator mixture can leach, elute, diffuse, bleed, discharge, desorb, dissolve, drain, seep, or leak from the coated proppant particulates at any suitable rate. According to one or more exemplary embodiments, the activator mixture can leach, elute, diffuse, bleed, discharge, desorb, dissolve, drain, seep, or leak from the coated proppant particulates at a rate of at least about 0.1 parts-per-million per gram of proppant particulates per day (expressed herein as ppm/(gram*day)), at least about 0.5 ppm/(gram*day), at least about 1 ppm/(gram*day), at least about 1.5 ppm/(gram*day), at least about 2 ppm/(gram*day), at least about 3 ppm/(gram*day), at least about 5 ppm/(gram*day), at least about 7 ppm/(gram*day), or at least about 10 ppm/(gram*day) for at least about 2 months, at least about 6 months, at least about 9 months, at least about 1 year, or at least about 2 years. For example, the activator mixture can

elute from the coated proppant particulates at a rate from about 0.01 ppm/(gram*day), about 0.075 ppm/(gram*day), about 0.1 ppm/(gram*day), about 0.25 ppm/(gram*day), about 0.75 ppm/(gram*day), about 1.5 ppm/(gram*day), about 2.25 ppm/(gram*day), or about 3 ppm/(gram*day) to about 4 ppm/(gram*day), about 5 ppm/(gram*day), about 6 ppm/(gram*day), about 7 ppm/(gram*day), about 8 ppm/(gram*day), about 9 ppm/(gram*day), about 10 ppm/(gram*day), about 20 ppm/(gram*day), about 30 ppm/(gram*day), or about 50 ppm/(gram*day) for at least about 2 months, at least about 6 months, at least about 9 months, at least about 1 year, or at least about 2 years.

The electromagnetic methods described herein can include electrically energizing the earth at or near a fracture at depth and measuring the electric and magnetic responses at the earth's surface or in adjacent wells/boreholes. The electromagnetic methods described herein can include energizing the earth in the fractured well/borehole or in a well/borehole adjacent to the fractured well/borehole. The electromagnetic methods described herein are can be used in connection with a cased wellbore, such as well **20** shown in FIG. **2**, or in an uncased wellbore (not shown). As shown in FIG. **2**, casing **22** extends within well **20** and well **20** extends through geological strata **24***a*-**24***i* in a manner that has three dimensional components.

Referring now to FIG. **3**, a partial cutaway view is shown with production well **20** extending vertically downward through one or more geological layers **24***a*-**24***i* and horizontally in layer **24***i*. While wells are conventionally vertical, the electromagnetic methods described herein are not limited to use with vertical wells. Thus, the terms "vertical" and "horizontal" are used in a general sense in their reference to wells of various orientations.

The preparation of production well **20** for hydraulic fracturing can include drilling a bore **26** to a desired depth and then in some cases extending the bore **26** horizontally so that the bore **26** has any desired degree of vertical and horizontal components. A casing **22** can be cemented **28** into well **20** to seal the bore **26** from the geological layers **24***a*-**24***i* in FIG. **3**. The casing **22** can have a plurality of perforations **30** and/or sliding sleeves (not shown). The perforations **30** are shown in FIG. **3** as being located in a horizontal portion of well **20** but those of ordinary skill in the art will recognize that the perforations can be located at any desired depth or horizontal distance along the bore **26**, but are typically at the location of a hydrocarbon bearing zone in the geological layers **24**, which may be within one or more of the geological layers **24***a*-**24***j*. Those of ordinary skill in the art will also recognize that the well **20** can include no casing, such as in the case of an open-hole well. The hydrocarbon bearing zone may contain oil and/or gas, as well as other fluids and materials that have fluid-like properties. The hydrocarbon bearing zone in geological layers **24***a*-**24***j* is hydraulically fractured by pumping a fluid into casing **22** and through perforations **30** at sufficient rates and pressures to create fractures **32** and then incorporating into the fluid an electrically conductive proppant which will prop open the created fractures **32** when the hydraulic pressure used to create the fractures **32** is released.

The hydraulic fractures **32** shown in FIG. **3** are oriented radially away from the metallic well casing **22**. This orientation is exemplary in nature. In practice, hydraulically-induced fractures **32** may be oriented radially as in FIG. **3**, laterally or intermediate between the two. Various orientations are exemplary and not intended to restrict or limit the electromagnetic methods described herein in any way.

The electrically conductive proppant can be introduced into one or more subterranean fractures during any suitable hydraulic fracturing operation to provide an electrically conductive proppant pack. In one or more exemplary hydraulic fracturing operations, any combination of the electrically conductive proppant and a non-electrically conductive proppant can be introduced into one or more fractures to provide an electrically conductive proppant pack. The electrically conductive proppant pack can include non-electrically conductive proppant in any suitable amounts. The non-electrically conductive proppant can have any suitable resistivity. For example, the non-electrically conductive proppant can have a resistivity of at least about 1×10^5 Ohm-cm, at least about 1×10^8 Ohm-cm, at least about 1×10^{10} Ohm-cm, at least about 1×10^{11} Ohm-cm, or at least about 1×10^{12} Ohm-cm. In one or more exemplary embodiments, the electrically conductive proppant pack can include at least about 1 wt %, at least about 5 wt %, at least about 10 wt %, at least about 20 wt %, at least about 40 wt %, at least about 50 wt %, at least about 60 wt %, at least about 70 wt %, at least about 80 wt %, at least about 90 wt %, or at least about 95 wt % non-electrically conductive proppant. In one or more exemplary embodiments, the electrically conductive proppant pack can include at least about 1 wt %, at least about 5 wt %, at least about 10 wt %, at least about 20 wt %, at least about 40 wt %, at least about 50 wt %, at least about 60 wt %, at least about 70 wt %, at least about 80 wt %, at least about 90 wt %, or at least about 95 wt % electrically conductive proppant. In one or more exemplary embodiments, the electrically conductive proppant pack can have an electrically conductive proppant concentration of about 2 wt %, about 4 wt %, about 8 wt %, about 12 wt %, about 25 wt %, about 35 wt %, or about 45 wt % to about 55 wt %, about 65 wt %, about 75 wt %, about 85 wt %, or about 95 wt % based on the total weight of the proppant pack. In one or more exemplary embodiments, the electrically conductive proppant pack can include from about 1 wt % to about 10 wt %, from about 10 wt % to about 25 wt %, about 25 wt % to about 50 wt %, from about 50 wt % to about 75 wt %, or from about 75 wt % to about 99 wt % non-electrically conductive proppant.

In one or more exemplary embodiments, once the proppant pack has been formed in the subterranean fracture(s), the conductive particles can elute from the electrically conductive particles and form onto the outer surfaces of each of the proppants in the proppant pack, thus forming an electrically conductive coating or electrically conductive outer shell onto each of the proppants in the proppant pack. In one or more exemplary embodiments, once the proppant pack has been formed in the subterranean fracture(s), the conductive particles can elute from the electrically conductive particles and form onto the outer surfaces of at least about 1 wt %, at least about 5 wt %, at least about 10 wt %, at least about 20 wt %, at least about 40 wt %, at least about 50 wt %, at least about 60 wt %, at least about 70 wt %, at least about 80 wt %, at least about 90 wt %, or at least about 95 wt % of the proppants in the proppant pack.

According to certain embodiments of the electromagnetic method of the present invention and as shown schematically in FIG. **4**, electric current is carried down wellbore **20** to an energizing point which will generally be located within 10 meters or more (above or below) of perforations **30** in casing **22** via a seven strand wire line insulated cable **34**, such as those which are well known to those of ordinary skill in the art and are widely commercially available from Camesa Wire, Rochester Wire and Cable, Inc., WireLine Works, Novametal Group, and Quality Wireline & Cable Inc. In

other exemplary embodiments, the wire line insulated cable 34 can contain 1 to 6 strands or 8 or more strands. A sinker bar 36 connected to the wire line cable 34 contacts or is in close proximity to the well casing 22 whereupon the well casing 22 becomes a current line source that produces subsurface electric and magnetic fields. In other exemplary embodiments, the wire line cable 34 can be connected to or otherwise attached to a centralizer and/or any other suitable downhole tool in addition to or in lieu of the sinker bar 26. These fields interact with the fracture 32 containing electrically conductive proppant to produce secondary electric and magnetic fields that will be used to detect, locate, and characterize the proppant-filled fracture 32.

According to certain embodiments of the electromagnetic method of the present invention and as shown schematically in FIG. 4, a power control box 40 is connected to casing 22 by a cable 42 so that electric current is injected into the fracture well 20 by directly energizing the casing 22 at the well head or any other suitable surface location. In one embodiment, the power control box 40 is connected wirelessly by a receiver/transmitter 43 to a receiver/transmitter 39 on equipment truck 41. Those of ordinary skill in the art will recognize that other suitable means of carrying the current to the energizing point may also be employed.

As shown schematically in FIGS. 4-6, a plurality of electric and magnetic field sensors 38 will be located on the earth's surface in a rectangular or other suitable array covering the area around the fracture well 20 and above the anticipated fracture 32. In one embodiment, the sensors 38 are connected wirelessly to a receiver/transmitter 39 on equipment truck 41. The maximum dimension of the array (aperture) in general should be at least 80 percent of the depth to the fracture zone. The sensors 38 will measure the x, y and z component responses of the electric and magnetic fields. It is these responses that will be used to infer location and characterization of the electrically conductive proppant through comparison to numerical simulations and/or inversion of the measured data to determine the source of the responses. The responses of the electric and magnetic field components will depend upon: the orientation of the fracture well 20, the orientation of the fracture 32, the electrical conductivity, magnetic permeability, and electric permittivity of layers 24a-24j, the electrical conductivity, magnetic permeability, and electric permittivity of the proppant filled fracture 32, and the volume of the proppant filled fracture 32. Moreover, the electrical conductivity, magnetic permeability and electric permittivity of the geological layers residing between the surface and the target formation layers 24a-24j influence the recorded responses. From the field-recorded responses, details of the proppant filled fracture 32 can be determined.

In another embodiment, electric and magnetic sensors may be located in adjacent well/boreholes.

Depending upon the conductivity of the earth surrounding the well casing 22, the current may or may not be uniform as the current flows back to the surface along the well casing 22. According to both embodiments shown in FIG. 4, current leakage occurs along wellbore 20 such as along path 50 or 52 and returns to the electrical ground 54 which is established at the well head. As described in U.S. patent application Ser. No. 13/206,041 filed Aug. 9, 2011 and entitled "Simulating Current Flow Through a Well Casing and an Induced Fracture," the entire disclosure of which is incorporated herein by reference, the well casing is represented as a leaky transmission line in data analysis and numerical modeling. Numerical simulations have shown that for a conducting earth (conductivity greater than approximately

0.05 siemens per meter (S/m)), the current will leak out into the formation, while if the conductivity is less than approximately 0.05 S/m the current will be more-or-less uniform along the well casing 22. As shown in FIGS. 7A and 7B, to localize the current in the well casing 22, electrically insulating pipe joints or pipe collars may be installed. According to the embodiment shown in FIG. 7A, an insulating joint may be installed by coating the mating surfaces 60 and 62 of the joint with a material 64 having a high dielectric strength, such as any one of the well-known and commercially available plastic or resin materials which have a high dielectric strength and which are of a tough and flexible character adapted to adhere to the joint surfaces so as to remain in place between the joint surfaces. As described in U.S. Pat. No. 2,940,787, the entire disclosure of which is incorporated herein by reference, such plastic or resin materials include epoxies, phenolics, rubber compositions, and alkyds, and various combinations thereof. Additional materials include polyetherimide and modified polyphenylene oxide. According to the embodiment shown in FIG. 7B, the mating ends 70 and 72 of the joint are engaged with an electrically insulated casing collar 74. The transmission line representation is able to handle various well casing scenarios, such as vertical only, slant wells, vertical and horizontal sections of casing, and, single or multiple insulating gaps.

The detection, location, and characterization of the electrically conductive proppant in a fracture will depend upon several factors, including but not limited to the net electrical conductivity of the fracture, fracture volume, the electrical conductivity, magnetic permeability, and electric permittivity of the earth surrounding the fracture and between the fracture and surface mounted sensors. The net electrical conductivity of the fracture means the combination of the electrical conductivity of the fracture, the proppant and the fluids when all are placed in the earth minus the electrical conductivity of the earth formation when the fracture, proppant and fluids were not present. Also, the total electrical conductivity of the proppant filled fracture is the combination of the electrical conductivity created by making a fracture, plus the electrical conductivity of the new/modified proppant plus the electrical conductivity of the fluids, plus the electro-kinetic effects of moving fluids through a porous body such as a proppant pack. The volume of an overly simplified fracture with the geometric form of a plane may be determined by multiplying the height, length, and width (i.e. gap) of the fracture. A three dimensional (3D) finite-difference electromagnetic algorithm that solves Maxwell's equations of electromagnetism may be used for numerical simulations. In order for the electromagnetic response of a proppant filled fracture at depth to be detectable at the Earth's surface, the net fracture conductivity multiplied by the fracture volume within one computational cell of the finite difference (FD) grid must be larger than approximately 100 Sm^2 for a Barnett shale-like model where the total fracture volume is approximately 38 m^3. For the Barnett shale model, the depth of the fracture is 2000 m. These requirements for the numerical simulations can be translated to properties in a field application for formations other than the Barnett shale.

The propagation and/or diffusion of electromagnetic (EM) wavefields through three-dimensional (3D) geological media are governed by Maxwell's equations of electromagnetism.

According to one embodiment of the present invention, the measured three dimensional components of the electric and magnetic field responses may be analyzed with imaging

methods such as an inversion algorithm based on Maxwell's equations and electromagnetic migration and/or holography to determine proppant pack location. Inversion of acquired data to determine proppant pack location involves adjusting the earth model parameters, including but not limited to the proppant location within a fracture or fractures and the net electrical conductivity of the fracture, to obtain the best fit to forward model calculations of responses for an assumed earth model. As described in Bartel, L. C., Integral wave-migration method applied to electromagnetic data, SEG Technical Program Expanded Abstracts, 1994, 361-364, the electromagnetic integral wave migration method utilizes Gauss's theorem where the data obtained over an aperture is projected into the subsurface to form an image of the proppant pack. Also, as described in Bartel, L. C., Application of EM Holographic Methods to Borehole Vertical Electric Source Data to Map a Fuel Oil Spill, SEG Technical Program Expanded Abstracts, 1987, 49-51, the electromagnetic holographic method is based on the seismic holographic method and relies on constructive and destructive interferences where the data and the source wave form are projected into an earth volume to form an image of the proppant pack. Due to the long wave lengths of the low frequency electromagnetic responses for the migration and holographic methods, it may be necessary to transform the data into another domain where the wave lengths are shorter. As described in Lee, K. H., et al., A new approach to modeling the electromagnetic response of conductive media, Geophysics, Vol. 54, No. 9 (1989), this domain is referred to as the q-domain. Further, as described in Lee, K. H., et al., Tomographic Imaging of Electrical Conductivity Using Low-Frequency Electromagnetic Fields, Lawrence Berkeley Lab, 1992, the wave length changes when the transformation is applied.

Also, combining Maxwell's equations of electromagnetism with constitutive relations appropriate for time-independent isotropic media yields a system of six coupled first-order partial differential equations referred to as the "EH" system. The name derives from the dependent variables contained therein, namely the electric vector E and the magnetic vector H. Coefficients in the EH system are the three material properties, namely electrical current conductivity, magnetic permeability, and electric permittivity. All of these parameters may vary with 3D spatial position. The inhomogeneous terms in the EH system represent various body sources of electromagnetic waves, and include conduction current sources, magnetic induction sources, and displacement current sources. Conduction current sources, representing current flow in wires, cables, and borehole casings, are the most commonly-used sources in field electromagnetic data acquisition experiments.

In one or more exemplary embodiments, an explicit, time-domain, finite-difference (TDFD) numerical method is used to solve the EH system for the three components of the electric vector E and the three components of the magnetic vector H, as functions of position and time. A three-dimensional gridded representation of the electromagnetic medium parameters, referred to as the "earth model" is required, and may be constructed from available geophysical logs and geological information. A magnitude, direction, and waveform for the current source are also input to the algorithm. The waveform may have a pulse-like shape (as in a Gaussian pulse), or may be a repeating square wave containing both positive and negative polarity portions, but is not limited to these two particular options. Execution of the numerical algorithm generates electromagnetic responses in the form of time series recorded at receiver locations distributed on or within the gridded earth model. These responses represent the three components of the E or H vector, or their time-derivatives.

Repeated execution of the finite-difference numerical algorithm enables a quantitative estimate of the magnitude and frequency-content of electromagnetic responses (measured on the earth's surface or in nearby boreholes) to be made as important modeling parameters are varied. For example, the depth of current source may be changed from shallow to deep. The current source may be localized at a point, or may be a spatially-extended transmission line, as with an electrically charged borehole casing. The source waveform may be broad-band or narrow-band in spectral content. Finally, changes to the electromagnetic earth model can be made, perhaps to assess the shielding effect of shallow conductive layers. The goal of such a modeling campaign is to assess the sensitivity of recorded electromagnetic data to variations in pertinent parameters. In turn, this information is used to design optimal field data acquisition geometries that have enhanced potential for imaging a proppant-filled fracture at depth.

The electric and magnetic responses are scalable with the input current magnitude. In order to obtain responses above the background electromagnetic noise, a large current on the order of 10 to 100 amps may be required. The impedance of the electric cable to the current contact point and the earth contact resistance will determine the voltage that is required to obtain a desired current. The contact resistance is expected to be small and will not dominate the required voltage. In addition, it may be necessary to sum many repetitions of the measured data to obtain a measurable signal level over the noise level. In the field application and modeling scenarios, a time-domain current source waveform may be used. A typical time-domain waveform consists of an on time of positive current followed by an off time followed by an on time of negative current. In other words, + current, then off, then − current, then off again. The repetition rate to be used would be determined by how long the current has to be on until a steady-state is reached or alternatively how long the energizing current has to be off until the fields have died to nearly zero. In this exemplary method, the measured responses would be analyzed using both the steady-state values and the decaying fields following the current shut-off. The advantage of analyzing the data when the energizing current is zero (decaying fields) is that the primary field contribution (response from the transmitting conductor; i.e., the well casing) has been eliminated and only the earth responses are measured. In addition, the off period of the time domain input signal allows analysis of the direct current electrical fields that may arise from electro-kinetic effects, including but not limited to, flowing fluids and proppant during the fracturing process. Fracture properties (orientation, length, volume, height and asymmetry will be determined through inversion of the measured data and/or a form of holographic reconstruction of that portion of the earth (fracture) that yielded the measured electrical responses or secondary fields. According to certain embodiments, a pre-fracture survey will be prepared to isolate the secondary fields due to the fracture. Those of ordinary skill in the art will recognize that other techniques for analyzing the recorded electromagnetic data, such as use of a pulse-like current source waveform and full waveform inversion of observed electromagnetic data may also be used.

In one or more exemplary embodiments, a frequency domain finite-difference (FDFD) numerical method is used to solve the EH system for the three components of the electric vector E and the three components of the magnetic

vector H. The earth model, magnitude, direction, and waveform for the current source can be inputted to the algorithm. Similar to that of the TDFD numerical method, the waveform may have a pulse-like shape (as in a Gaussian pulse), or may be a repeating square wave containing both positive and negative polarity portions, but is not limited to these two particular options. Execution of the numerical algorithm generates electromagnetic responses in the form of frequency series recorded at receiver locations distributed on or within the gridded earth model. These responses represent the three components of the E or H vector, or their frequency-derivatives.

In one or more exemplary embodiments, an induced polarization (IP) effect is used to determine a location of the proppant. The IP effect is present in the time domain where the effect is measured flowing the cessation of the driving electric field. The IP effect is also present in the frequency domain wherein the effect is explained in terms of complex impedance. For time domain measurements the received voltage decay as a function of time is made when the input current is off. The frequency domain measures the phase delay from the input current and the effects of frequency on the received voltage.

The IP effect arises from various causes and different dependencies on the frequency of an impressed electric field. Central to some of the theories is fluid flow in porous media. In a porous medium the earth material is generally slightly negatively charged, thereby attracting positive charged ions in the fluid that makes up the electric double layer (EDL). This leaves the fluid in the pore space somewhat rich in negative charges that now conduct current in a porous medium. The ionic current is the difference in the concentrations of positive and negative ions. The flow of ions takes place due to an impressed electric field, pressure gradient, and/or diffusion where the pore space available for transport is restricted by the EDL. In addition, there are other restrictions for flow (pore throats, other material in the pore space) that can cause charge build up. A metallic ore, which is an electronic conductor, also affects the flow of the ions. Once the forcing electric field is switched off, the charge distribution "wants" to seek a lower energy state, which is the equilibrium condition. Diffusion of charges plays a major role in the quest to obtain equilibrium. In other words, when a surface is immersed or created in an aqueous solution, a discontinuity is formed at the interface where such physico-chemical variables as electric potential and electrolyte concentration change significantly from the aqueous phase to another phase. Because of the different chemical potentials between the two phases, charge separation often occurs at the interfacial region. This interfacial region, together with the charged surface, is usually known as the EDL. This EDL, or layer, which can extend as far as 100 nm in a very dilute solution to only a few angstroms in a concentrated solution, plays an important role in electrochemistry, colloid science, and surface chemistry (Devasenathipathy and Santiago, 2003; Kirby and Hasselbrink, 2004; Yang et al., 2004).

Once the conducting proppant has been placed into the fracture(s) and an electric current is supplied to the well casing, the component of the electric field perpendicular to the direction of the fracture will generally be larger than the component parallel to the fracture. The component of the electric field parallel to the fracture will induce ionic conductivity in the fracture fluid that will be impeded due to the ion mobility in the presence of the EDL and the charges induced on the conductive proppant. In addition, there will be electronic current flow via electrically conductive proppant that are in contact with each other. The current flow

perpendicular to the fracture will not depend appreciably on the ionic flow but more on electronic conduction via the metallic coated proppant particles. The electronic conduction of electrical current will depend on the volume of the metal present and will rely on proppant particles to be in contact with each other.

If the energizing current is on for a sufficient amount of time so that the movement of charges has reached a steady state in the presence of the applied electric field, then when the current is terminated and the applied electric field goes to zero the charges must redistribute themselves to come to an equilibrium charge distribution. This redistribution does not occur instantaneously, but involves several decay mechanisms. Membrane IP effects can occur along with the electrode polarization effect. Conductive coatings and/or conductive particles present at or on the proppant surface can produce a significant IP response through the chargeability that is related to the surface impedance term. The surface impedance term will have some time (or frequency) dependent decay characteristic. This IP response from the conductive proppant particles will depend upon the total surface area of these proppant particles. For example, for a 1 micron thick metallic coating on a proppant particle substrate having a diameter 700 microns, the volume of metallic coating is approximately 15×10^{13} m^3 and the surface are per proppant particle is 1.54×10^{-6} m^2. A 75% packing factor, for example, would mean 4.14×10^9 proppant particles per unit volume, where the total volume of metal is 0.0062 per cubic meter while the total surface area is 6380 per cubic meter. This calculation shows that the IP effect due to the metallic coated proppant particles can be greater than the enhanced conductivity effect of the metallic coated proppant particles.

Another EM response that impacts IP measurements is the inductive response of the earth. The inductive response arises from the Faraday/Lentz law which produces eddy currents in conductive media. The response is based upon the time-rate-of-change of the magnetic field; if the magnetic field is increasing, eddy currents are generated in the conductor (earth) to create a magnetic field opposite to the increasing magnetic field, and if the magnetic field is decreasing eddy currents are generated in the conductor to create a magnetic field opposite that of the decreasing magnetic field. The result of this is to produce a response much like the IP response; i.e., after a turn on of a primary magnetic field (turning on the current), the response takes time to achieve saturation and following the turn off of the primary magnetic field (turning off the current) the response slowly decays to zero. Along with the surrounding conducting earth, the conducting fracture (fluid and proppant) will generate an inductive response in addition to the IP response discussed above. Due to the coupling of electric and magnetic field through Maxwell's equations, the magnetic induction manifests itself in the electric field as well. The inductive and IP effects are additive. These two responses can be separated in the magnetic field due to their different frequency responses.

Also, the finite-difference solutions to Maxwell's equations, FDEM, includes the inductive responses, but not the IP responses. In one or more exemplary embodiments, the IP effects can be included into the FDEM algorithm by treating the IP effect as a time dependent source term. If the IP effect is treated as a time dependent source term, then the IP effect can be much larger than the pure conductive response.

A field data acquisition experiment was conducted to test the transmission line representation of a well casing current source. The calculated electric field and the measured elec-

tric field are in good agreement. This test demonstrates that the transmission line current source implementation in the 3D finite-difference electromagnetic code gives accurate results. The agreement, of course, depends upon an accurate model describing the electromagnetic properties of the earth. In this field data acquisition experiment, common electrical logs were used to characterize the electrical properties of the earth surrounding the test well bore and to construct the earth model.

The following examples are included to demonstrate illustrative embodiments of the present invention. It will be appreciated by those of ordinary skill in the art that the techniques disclosed in these examples are merely illustrative and are not limiting. Indeed, those of ordinary skill in the art should, in light of the present disclosure, appreciate that many changes can be made in the specific embodiments that are disclosed, and still obtain a like or similar result without departing from the spirit and scope of the invention.

Example 1

Conventional low density and medium density ceramic proppants which are commercially available from CARBO Ceramics, Inc. of Houston, Tex. under the trade names CARBOLite (CL) 20/40, HydroProp 40/80, CARBOProp 20/40 and CARBOProp 40/70 were coated with thin layers of metals using RF magnetron sputtering. Three metal targets were used for the depositions, namely aluminum, copper and nickel. The depositions were performed in a sputter chamber using a 200 W RF power, a deposition pressure of 5 mTorr, and an argon background (90 sccm). The sputter chamber had three articulating 2 inch target holders that can be used to coat complex shapes. The system also had a rotating water-cooled sample stage that was used in a sputter-down configuration. Prior to coating the proppants, deposition rates for the three metals were determined by sputtering the metals onto silicon wafers and measuring the coating thickness by scanning electron microscope (SEM) cross-sectional analysis with a Zeiss Neon 40 SEM.

The proppants were loaded into the sputter chamber in a 12 inch diameter aluminum pan with 1 inch tall sides. Approximately 130 g of proppant was used for each coating run. This amount of proppant provided roughly a single layer of proppant on the base of the pan. The proppant was "stirred" during the deposition using a 6 inch long fine wire metal that was suspended above the pan and placed into contact with the proppant in the pan. The coating deposition times were doubled compared to what was determined from the silicon wafer coating thickness measurements to account for roughly coating the proppants on one side, rolling them over, and then coating the other side. Coatings of approximately 100 nm and approximately 500 nm were deposited on each type of proppant with each of the three metals.

Following the coating process, the proppant was inspected visually and by optical microscopy. The results indicated that the proppant having a thinner coating of approximately 100 nm had a generally non-uniform coating while the proppant with the thicker coating of approximately 500 nm had a uniform coating.

Example 2

Conventional low density ceramic proppants which are commercially available from CARBO Ceramics, Inc. of Houston, Tex. under the trade names of CARBOLite 20/40 and HydroProp 40/80 were coated with thin layers of a conductive polymer using a planetary bench mixer with a

"B" flat beater and a heating mantle. Approximately 500 g of proppant was used for each coating run. Coatings of 0.1% by weight and 0.4% by weight of the proppant were prepared as shown in Table I below:

TABLE I

Conductive polymer	0.1% coating	0.4% coating
PEDOT:PSS Obtained from Sigma-Aldrich as a 1.2% solution in water	42 g	167 g
PANI Obtained from Sigma-Aldrich in an emeraldine base, as a 5% solution in tetrahydrofuran (THF) and doped with a 4-dodecylbenzene sulfonic acid in a 1:1 molar ratio	10 g	40 g
PPY Obtained from Sigma-Aldrich as a doped 5% dispersion in water	10 g	40 g

In each case, the proppant was heated to a temperature of 150-200° C. in an oven and was added to a steel mixing bowl. An adhesion promoter, such as aminopropyl triethoxy silane, an amino-functional coupling agent, and glycidyloxypropyl trimethoxy silane, a functional organosilane coupling agent, was added to the heated proppant to enhance the bond between the inorganic substrate and the organic polymer. The mixing bowl was set in an external heating mantle to allow the heat to remain in the system as additives were added. The "B" flat beater traveled along the side of the wall surfaces of the mixing bowl in circular orbits at an intermediate speed of approximately 280 rpm while the mixing bowl stayed in place, thereby allowing complete mixing in a short time. A typical batch schedule is shown in Table II below:

TABLE II

Coating Schedule on Ceramics:	
Ingredient	Time of Addition
Substrate	0 s
Adhesion Promoter	7 s
Conductive Polymer	15 s
End Cycle	5-10 min

Additionally, 0.1% and 0.4% coatings were made by adding PEDOT:PSS to a phenol-formaldehyde (Novolac) coating using a planetary mixer with "B" flat beater and a heating mantle as described above. Approximately 500 g of proppant was used for each coating run. For a 0.1% and 0.4% by weight coating of the proppant, approximately 42 g and 167 g of PEDOT:PSS, respectively, were added to 500 g of proppant with 20 g of phenol-formaldehyde (Novolac) resin cross-linked with hexamine (13% hexamine based on phenol-formaldehyde (Novolac) resin) with and without adhesion promoters as mentioned above. A typical batch schedule is shown in Table III below:

TABLE III

Coating Schedule on Ceramics with Phenol-Formaldehyde Resin:	
Ingredient	Time of Addition
Substrate	0 s
Phenol-Formaldehyde resin	0 s
Adhesion Promoter	7 s

TABLE III-continued

Coating Schedule on Ceramics with Phenol-Formaldehyde Resin:	
Ingredient	Time of Addition
Hexamine (cross-linker)	30 s
Conductive Polymer	1.5-2 min
End Cycle	5-10 min

Following the coating process, the coated proppant samples were inspected visually and by optical microscopy.

Example 3

The electrical conductivity of various proppant samples prepared according to Examples 1 and 2 as well as uncoated proppant samples was measured using the test device shown in FIG. **8**. As shown in FIG. **8**, the test system **200** included an insulating boron nitride die **202**, having an inside diameter of 0.5 inches and an outside diameter of 1.0 inches, disposed in a bore **204** in a steel die **206** in which the bore **204** had an inside diameter of 1.0 inches. Upper and lower steel plungers **208** and **210** having an outside diameter of 0.5 inches were inserted in the upper and lower ends **212**, **214**, respectively, of the insulating boron nitride die **202** such that a chamber **216** is formed between the leading end **218** of the upper plunger **208**, the leading end **220** of the lower plunger **210** and the inner wall **222** of the boron nitride sleeve **202**. Upper plunger **208** was removed from the insulating boron nitride die **202** and proppant was loaded into the chamber **216** until the proppant bed **224** reached a height of about 1 to 2 cm above the leading end **220** of the lower plunger **210**. The upper plunger **208** was then reinstalled in the insulating boron nitride die **202** until the leading end **218** of the upper plunger **208** engaged the proppant **224**. A copper wire **226** was connected to the upper plunger **208** and one pole of each of a current source **228** and a voltmeter **230**. A second copper wire was connected to the lower plunger **210** and the other pole of each of the current source **228** and the voltmeter **230**.

suitable voltmeter well known to those of ordinary skill in the art such as a Fluke 175 True RMS Multimeter which may be used in the DC mV mode for certain samples and in the ohmmeter mode for higher resistance samples.

The current source was powered on and the resistance of the test system **200** with the proppant bed **224** in the chamber **216** was then determined. The resistance of the proppant **224** was then measured with the Multimeter as a function of pressure using the upper plunger **108** and lower plunger **110** both as electrodes and to apply pressure to the proppant bed **224**. Specifically, $R=V/I$—the resistance of the system with the plungers touching is subtracted from the values measured with the proppant bed **224** in the chamber **216** and the resistivity, $\rho=R*A/t$ where A is the area occupied by the proppant bed **224** and t is the thickness of the proppant bed **224** between the upper plunger **108** and the lower plunger **110**.

The results were as follows:

Electrical measurements of base proppants without the addition of any conductive material were conducted at 100 V DC on samples that were 50 volume % proppant in wax that were pressed into discs nominally 1 inch in diameter and approximately 2 mm thick. Using these values to calculate the resistivity and using the measured resistivity for pure wax, the values below were extrapolated by plotting log (resistivity) vs. volume fraction proppant and extrapolating to a volume fraction of one:

CarboProp 40/70: 2×10^{12} Ohm-cm
CarboProp 20/40: 0.6×10^{12} Ohm-cm
CarboHydroProp: 1.8×10^{12} Ohm-cm
CarboEconoProp: 9×10^{12} Ohm-cm

It should be noted that the resistivities of the samples measured above are very high and not suitable for detection in the present invention.

Electrical measurements of base proppants with coatings of aluminum in thicknesses of 100 nm and 500 nm prepared according to Example 1, and base proppants with coatings of 0.1% or 0.4% of poly(3,4-ethylenedioxythiophene) (PEDOT), with or without amino silane were conducted. The results are shown in Table IV below and FIG. **9**.

TABLE IV

	Resistivity (ohm-cm)				
Description	0 psi	1500 psi	2500 psi	3000 psi	5000 psi
Base Material-no coating/no modification	9×10^{12}	Not measured	Not measured	Not measured	Not measured
CL w/0.1% PEDOT	Not measured	1000 to 5000	1000 to 5000	1000 to 5000	1000 to 5000
CL w/0.1% PEDOT/ amino silane	Not measured	10,000 to 100,000	10,000 to 50,000	10,000 to 25,000	Not measured
CL w/0.4% PEDOT	Not measured	1000 to 5000	1000 to 5000	1000 to 5000	1000 to 5000
CL w/0.4% PEDOT/ amino silane	Not measured	5000 to 10,000	~5000	~5000	Not measured
CL w/100 nm Al coat	Not measured	1,000	1,000	1,000	Not measured
CL w/500 nm Al coat	5 to 10	~0	0.1-0	0.1-0	0.1-0
CL w/500 nm Al coat	Not measured	~0	0.27	Not measured	Not measured
HP w/100 nm Al coat	Not measured	>1,000,000	>1,000,000	>1,000,000	>1,000,000
HP w/500 nm Al coat	Not measured	0-1	0.30	0-1	0-1

The current source may be any suitable DC current source well known to those of ordinary skill in the art such as a Keithley 237 High Voltage Source Measurement Unit in the DC current source mode and the voltmeter may be any

As can be seen from FIG. **9**, the best results in terms of conductivity were obtained with CarboLite (CL) 20/40 and HydroProp (HP) 40/80 having a 500 nm thick coating of aluminum.

Electrical measurements of mixtures of base proppants with varying percentages of such base proppants with coatings of aluminum in thicknesses of 500 nm prepared according to Example 1 were conducted. The results are shown in Tables V and VI below and FIGS. **10-11**.

Table V shows data for mixtures of CarboLite 20/40 with a 500 nm coating of aluminum and CarboLite 20/40 with no added conductive material. For each sample shown in Table V, 3 g. of the sample material was placed in the 0.5 inch die to provide an area of 0.196 square inches. The applied current for each test was 5 mA and the tests were conducted at room temperature.

TABLE V

Load (lbs)	Pressure (psi)	Voltage (mV)	Resistance (Ohm)	Resistivity (Ohm-cm)
80% 500 nm Al-coated CarboLite with 20% CarboLite 20/40				
100	509	6.1	1.22	1.107
200	1019	5.6	1.12	1.016
300	1528	5.0	1.00	0.907
400	2037	4.7	0.94	0.853
500	2546	4.5	0.90	0.817
60% 500 nm Al-coated CarboLite with 40% CarboLite 20/40				
200	1019	20.0	4.00	3.630
300	1528	17.8	3.56	3.230
400	2037	17.0	3.40	3.085
500	2546	16.1	3.22	2.922
600	3056	15.8	3.16	2.867
40% 500 nm Al-coated CarboLite with 60% CarboLite 20/40				
100	509	253	50.60	46.516
200	1019	223	44.60	41.000
300	1528	218	43.60	40.080
400	2037	226	45.20	41.552
500	2546	221	44.20	40.632

Table VI shows data for mixtures of HydroProp 40/80 with a 500 nm coating of aluminum and HydroProp 40/80 with no added conductive material. For each sample shown in Table VI, 3 g. of the sample material was placed in the 0.5 inch die to provide an area of 0.196 square inches. The applied current for each test was 5 mA and the tests were conducted at room temperature.

TABLE VI

Load (lbs)	Pressure (psi)	Voltage (mV)	Resistance (Ohm)	Resistivity (Ohm-cm)
80% 500 nm Al-coated HydroProp 40/80 with 20% HydroProp 40/80				
100	509	5.9	1.18	1.083
200	1019	5.3	1.06	0.973
300	1528	4.9	0.98	0.900
400	2037	4.6	0.92	0.845
500	2546	4.4	0.88	0.808
60% 500 nm Al-coated HydroProp 40/80 with 40% HydroProp 40/80				
200	1019	17.5	3.50	3.167
300	1528	15.6	3.12	2.823
400	2037	14.5	2.90	2.624
500	2546	13.8	2.76	2.497
40% 500 nm Al-coated HydroProp 40/80 with 60% HydroProp 40/80				
200	1019	550	110.00	99.532
300	1528	470	94.00	85.055
400	2037	406	81.20	73.473
500	2546	397	79.40	71.844

As can be seen from TABLES V and VI as well as FIGS. **10-11**, the resistivity of the proppant packs, regardless of the

relative amounts of coated or un-coated proppant, tends to decrease with increasing closure pressure. In addition, as the relative amount of uncoated proppant increases and the relative amount of coated proppant decreases, the resistivity of the proppant packs increases dramatically. Lastly, the lowest resistivity is achieved with 100% Al-coated proppant. No mixture of coated and uncoated proppant results in a resistivity measurement less than 100% Al-coated proppant.

When used as a proppant, the particles described herein may be handled in the same manner as conventional proppants. For example, the particles may be delivered to the well site in bags or in bulk form along with the other materials used in fracturing treatment. Conventional equipment and techniques may be used to place the particles in the formation as a proppant. For example, the particles are mixed with a fracture fluid, which is then injected into a fracture in the formation.

In an exemplary method of fracturing a subterranean formation, a hydraulic fluid is injected into the formation at a rate and pressure sufficient to open a fracture therein, and a fluid containing sintered, substantially round and spherical particles prepared from a slurry as described herein and having one or more of the properties as described herein is injected into the fracture to prop the fracture in an open condition.

The foregoing description and embodiments are intended to illustrate the invention without limiting it thereby. It will be understood that various modifications can be made in the invention without departing from the spirit or scope thereof.

What is claimed is:

1. An electrically conductive proppant particle, comprising:
   a sintered, substantially round and spherical particle having less than about 30% crush at 4,000 psi and a specific gravity of about 3.8 g/cm^3 or less; and
   a plurality of conductive particles,
   wherein the sintered, substantially round and spherical particle has one or more pores and at least one of the plurality of conductive particles is disposed within at least one of the one or more pores,
   wherein the at least one of the plurality of conductive particles is mixed with an activator to provide an activator mixture that is infused into the one or more pores, and
   wherein the activator mixture elutes from the one or more pores so that the at least one conductive particle is located at a surface of the electrically conductive proppant particle after the electrically conductive proppant particle has been introduced to a subterranean fracture.

2. The electrically conductive proppant particle of claim 1, wherein the sintered, substantially round and spherical particle is selected from the group consisting of ceramic proppant, sand, plastic beads and glass beads.

3. The electrically conductive proppant particle of claim 1, wherein the conductive particles comprise iron, silver, gold, copper, aluminum, calcium, tungsten, zinc, nickel, lithium, platinum, tin, or carbon steel, or any combination or oxide thereof.

4. The electrically conductive proppant particle of claim 1, wherein the conductive particles comprise graphite, graphene, single-walled carbon nanotubes or double-walled carbon nanotubes.

5. The electrically conductive proppant particle of claim 1, wherein the conductive particles further comprise an outer coating comprising one or more chemicals or ligands that impart surface functionality to the conductive particles so

that the conductive particles have an affinity for an outer surface of the electrically conductive proppant.

6. The electrically conductive proppant particle of claim 1, wherein at least a portion of the plurality of the conductive particles is mixed with a resin coating encapsulating the sintered, substantially round and spherical particle.

7. The electrically conductive proppant particle of claim 1, wherein the electrically conductive proppant particle has a conductive particle content of from about 0.1% to about 10% by weight.

8. The electrically conductive proppant particle of claim 1, wherein the at least one of the plurality of conductive particles elutes from the at least one of the one or more pores after the electrically conductive proppant particle has been introduced to a subterranean fracture.

9. A proppant pack, comprising:

a first proppant component comprising a first plurality of sintered, substantially round and spherical particles and a plurality of conductive nanoparticles, wherein the first plurality of sintered, substantially round and spherical particles have an apparent specific gravity of about 3.8 g/cm^3 or less; and

a second proppant component comprising a second plurality of sintered, substantially round and spherical particles, the second proppant component having a resistivity of at least about 1×10^5 Ohm-cm,

wherein the conductive nanoparticles further comprise an outer coating comprising one or more chemicals or ligands that impart surface functionality to the conductive nanoparticles so that the conductive nanoparticles have an affinity for outer surfaces of the first proppant component and the second proppant component,

wherein the at least one of the plurality of conductive nanoparticles elutes from the first plurality of sintered, substantially round and spherical particles and contacts an outer surface of the second proppant component forming an electrically conductive shell on the outer surface of the second proppant component.

10. The proppant pack of claim 9, wherein the conductive nanoparticles comprise iron, silver, gold, copper, aluminum, calcium, tungsten, zinc, nickel, lithium, platinum, tin, or carbon steel, or any combination or oxide thereof.

11. A proppant pack, comprising:

a first proppant component comprising a first plurality of sintered, substantially round and spherical particles and a plurality of conductive nanoparticles, wherein the first plurality of sintered, substantially round and spherical particles have an apparent specific gravity of about 3.8 g/cm^3 or less; and

a second proppant component comprising a second plurality of sintered, substantially round and spherical particles, the second proppant component having a resistivity of at least about 1×10^5 Ohm-cm,

wherein the first plurality of sintered, substantially round and spherical particles comprises one or more pores and at least one of the plurality of conductive nanoparticles is disposed within at least one of the one or more pores,

wherein the at least one of the plurality of conductive nanoparticles is mixed with an activator to provide an activator mixture that is infused into the one or more pores, and

wherein the activator mixture elutes from the one or more pores so that the at least one conductive nanoparticle is located at a surface of the first proppant component.

12. The proppant pack of claim 11, wherein the conductive nanoparticles comprise iron, silver, gold, copper, aluminum, calcium, tungsten, zinc, nickel, lithium, platinum, tin, or carbon steel, or any combination or oxide thereof.

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